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ION-MIGRATION IN SOIL

by

ARVIND SHANKAR PATIL, B.Sc., M.S.A.

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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UNIVERSITY OF ALBERTA  
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Ion-migration in soil" submitted by Arvind Shankar Patil, B.Sc., M.S.A., in partial fulfilment of the requirements for the degree of Doctor of Philosophy.





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## ABSTRACT

The objective of the present study was the elucidation of the mechanism of ion-migration in soil.

The measurements of self-diffusion, electrical conductance, transport number, and electroosmosis were taken on an equilibrated two phase system of soil and electrolyte solution. Using the Nernst-Einstein relation, mobilities of Rubidium and Chloride ions in soil were determined from electrical and diffusion measurements. Activation energies for diffusion of Rubidium and Chloride ions in soil were also determined from diffusion measurements. Mean molal activity coefficients of RbCl in the soil phase were determined by the use of Donnan-equilibrium as a function of the concentration of the solution phase.

The reduction in the diffusion coefficients of Rubidium and Chloride ions in soil compared to that in solution, was accounted for on the basis of tortuosity of the path and the electrostatic interaction of the ionic species with the charged surfaces of soil. By means of simultaneous self-diffusion of  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  (whose concentrations were determined from the composite sample by making use of their radiation characteristics) effects of tortuosity and electrostatic interaction were isolated. The effect of electrostatic interaction was shown to correspond to the mean molal activity coefficient of RbCl in the soil phase within  $\pm 0.8\%$ .

Transport numbers of Rubidium in the soil were measured at various concentrations of solution phase. The objective was to determine



the range of concentration, where the soil plug behavior approaches that of the ideal permselective membrane. Over this range of concentration, it was shown that the potentials developed in a concentration cell, where the soil plug separated solutions of known activities, were approximately those predicted by the Teorell-Myers and Sievers theory of membrane potential.

Quasi-thermodynamic findings of earlier workers on single ion activity coefficients in colloidal systems, were confirmed by strictly thermodynamic means, suggesting the validity of such measurements. By the use of thermodynamics of irreversible processes, phenomenological coefficients were determined for transport processes in soil.





## Chapter 1.

### LITERATURE REVIEW AND FORMULATION OF PROBLEM

#### 1. Introduction

The study of ion-migration in soil is of primary interest from the point of view of plant nutrition. Its academic value, however, cannot be overemphasized. The advent of the nuclear age has brought forth the necessity of learning more about the transport of radioactive substances in soil, although the importance of movements of salts from the ground water has long been recognized.

The movement of ions in soil is affected by electrical interactions of the ions with the colloidal part of the soil which brings about many physicochemical changes including that of ion exchange. Because the colloidal part of the soil is interspersed between relatively inert particles of silt and sand and also between various forms of organic matter, it belongs to the general group of porous materials. The term porous media applies (Helfferich, 1962) to all types of systems consisting of a coherent but not necessarily rigid, structural framework with interstices ("pores") which are sufficiently wide to permit diffusion and other mass-transfer processes to take place in the media. The colloidal inorganic part of the soil consists of plate-shaped clay minerals having a residual charge as a result of isomorphic substitution in the lattice structure. The colloidal particles of organic matter are also present and exhibit numerous dissociable groups. Porous materials of various kinds show in different degrees the phenomenon of ion exchange. For



some the ion exchange capacity has a fixed value independent of ionic concentrations in the external solution; for others it is dependent on the concentration of a particular ion such as hydrogen.

In the process of exchange, ions suffer changes in electrical potential. Cationic exchangers made of sulfonated polymer typify one extreme case. Here the negatively charged sulfonate groups are fixed to a mesh of hydrocarbon chains which is permeated with water. As the exchangeable ions move through this molecular pore-space during thermal agitation, they suffer alternate fluctuations in electrical potential. However, as long as the sulfonate groups are fairly evenly spaced in three dimensions, these fluctuations will be no greater than in an aqueous solution of a simple electrolyte of comparable concentration. Another extreme case is typified by the exchanger in the form of clay micelles, which consists of solid particles into which the exchangeable ions cannot penetrate. Even if there are fixed charges distributed through the volume of the particle, as may be the case in Kaolinite, the counterions can only be crowded against the surfaces of the particle forming the so-called "diffuse double layer of counterions", which normally are replaceable.

The surface charge of the clay particles, surrounded by electrolytic solution, is due to (1) proton dissociation of the exposed OH groups and (2) isomorphic substitution of ions in the crystal lattice which have a valence differing from those of the ions proper to the lattice. The surface charge, as a result of the first mechanism, would be determined by the activity of  $H^+$  and the electrolytic concentration of ambient solution



as the system moves towards an equilibrium between the adsorbed protons and the protons in solution. On the other hand the surface charge due to the second mechanism is more or less fixed as a result of equilibrium reached during the formation of the clay lattice. Since OH groups are always present in the clay mineral along the planes of fracture, the dissociation charge will always be present. However, this will be affected by the substitution charge since it creates a negative surface potential in the clays which would suppress proton dissociation of neighboring groups and stimulate proton association (Bolt, 1960). The fact that for montmorillonite and illites the exchange capacity remains practically constant at different electrolytic levels in the pH range of 4 - 8 indicates that the substitution mechanism is the main cause of the charge carried by clay particles.

## 2. Methods used in the study of surface properties of clays

In the elucidation of physico-chemical properties of colloidal clay much research has been done on suspensions of colloidal clays. Thermodynamic, quasi-thermodynamic and irreversible thermodynamic approaches have so far been used (Marshall, 1956). Thermodynamic methods include (1) a study of the colligative properties -- vapour pressure lowering, freezing point depression etc. -- which measure the chemical potential of the water; (2) methods which measure or make use of chemical potential of molecular species; (3) measurement of energy transformations in clay systems. In quasi-thermodynamical methods electrochemical cells with liquid junctions are used. These





methods assume that the liquid junction potential in the clay suspension is negligible and that the presence of highly charged colloid does not affect the mobility of the potassium and chloride ions in the salt bridge. Therefore conclusions can be drawn regarding individual ions in their relation to clay particles. Conductance and diffusion measurements in homoionic systems are the irreversible thermodynamical methods used.

### 3. Ions in solution and forces involved in their migration

No single approach to the electrochemistry of soil colloids has gained complete acceptance in the literature at the present time. Of the two models in vogue one assumes that a suspension of clay particles can be treated by methods applicable to homogeneous solutions of electrolytes; whereas the other resorts to the concept of a two phase system of insoluble solid particles in an aqueous electrolytic solution.

This study is based on the two phase model. The soil phase is considered to consist of all the solid particles including the diffuse double layers of cations which are adsorbed on the particle surface against its residual charges. The solution phase consists of the aqueous electrolyte surrounding the soil phase. The colloidal particles of clay are many times larger than the ions. They, along with the diffused layer of adsorbed ions, are essentially a number of islands of high concentration of ions dispersed in a solution of much lower concentration rather than a part of a completely homogeneous system. In an ionic solution the electrostatic forces tend to bring the ions of opposite charge together while the thermal forces are dispersive. The combination of these two



effects was shown by Debye and Huckel (1923, 1924) to lead to the formation of ionic atmospheres where each positive ion, by inducing a negative charge density in its neighborhood, will be surrounded by an atmosphere which contains on the average more negative and less positive ions than in the bulk of the solution. Similarly a negative ion will be surrounded by a positive atmosphere. The whole charge of the ionic atmosphere is  $Z_i e$  where  $e$  is the electronic charge and  $Z_i$  is the valence of species  $i$ . It is equal in magnitude and opposite in sign to that of the central ion itself. It has been shown by the above workers that the effect of the ionic atmosphere is equivalent to that of a single charge of the same magnitude placed at a distance  $1/\kappa$  from the ion, where  $\kappa$  is defined by

$$\kappa = \left( \frac{4\pi e^2}{\epsilon kT} \sum n_i Z_i^2 \right)^{\frac{1}{2}} \quad (1-1)$$

where  $n$  is the number of ions of type  $i$  in unit volume,  $\epsilon$  is the dielectric constant,  $T$  is the absolute Temperature and  $k$  is Boltzman's constant. The quantity  $1/\kappa$  is regarded as a measure of the thickness of the ionic atmosphere. Taking  $n_i = c_i \frac{N}{1000}$  where  $c_i$  is the concentration of ions of type  $i$  in moles per liter and  $N$  is Avogadro's number, we get from Equ. 1-1

$$\frac{1}{\kappa} = \left( \frac{\epsilon T}{\sum c_i Z_i^2} \cdot \frac{1000k}{4\pi e^2 N} \right)^{\frac{1}{2}} \quad (1-2)$$

For water as solvent at  $25^\circ$ ,  $\epsilon = 78.6$  and with  $T = 298^\circ$ ,  $k = 1.38 \times 10^{-16}$  erg deg $^{-1}$ ,  $e = 4.802 \times 10^{-10}$  e. s. units and  $N = 6.025 \times 10^{23}$  we get

$$\frac{1}{\kappa} = \frac{4.31 \times 10^{-8}}{(\sum c_i Z_i^2)^{\frac{1}{2}}} \text{ cm.} \quad (1-3)$$



Thus the thickness of the ionic atmosphere is seen to be of the order of  $10^{-8}$  cm. and it decreases with increasing concentration and increasing valence of the ion present in the electrolyte. It increases with increasing dielectric constant of the solvent and with increasing temperature. The values of  $1/\kappa$  for a uni-univalent electrolyte at 0.1, 0.01 and 0.001 M are 9.64, 35.5 and 96.4 Å<sup>0</sup> respectively. Interaction between the ions, as manifested by the activity coefficient, is the result of the formation of an ionic atmosphere around each ion, which superficially seen, looks like micro-disturbances in a homogeneous system (Bolt, 1960). In actual effect, this presence of ionic rearrangement brings about a more uniform distribution. Since each ion tends to accumulate the oppositely charged neighbors, the result is a distribution of ions which resembles the beginning of a lattice type arrangement as in a NaCl crystal, where a Na ion is surrounded by Cl ions. In the neighborhood of a highly charged colloidal particle, the concentration of co-ions (anions) is virtually negligible in comparison to that of the counterions (cations). The atmosphere of oppositely charged ions around the central ion is totally absent in the neighborhood of a colloidal particle and the distribution of ions consists of more regular spacings of ion of the same sign. For surface potentials of less than 25 mv. Verway and Overbeek (1948) have shown that  $1/\kappa$  still retains its significance, namely that of designating the thickness of the double layer. The above considerations justify the use of the two phase model rather than treating the soil colloid and the ambient solution as a single homogeneous phase. The mechanism of







ion-migration in dilute solution is fairly accurately known and logically forms the basis of any treatment of ion-migration in soil. When an ion is moving in solution, the atmosphere surrounding the ion is not symmetrical, the charge density being greater behind than in front. Since the net charge of the atmosphere is opposite to that of the central ion, this atmosphere has spherical symmetry when the central ion is not moving. If the ion moves to the right, it will constantly have to build up its ionic atmosphere to the right, while the charge density to the left gradually decays. The rate at which the atmosphere to the right forms and that to the left dies is expressed in terms of time of relaxation of the ionic atmosphere. The asymmetry of the ionic atmosphere due to the time of relaxation will result in a retardation of ionic velocity and is known as the relaxation or asymmetry effect. The relaxation force opposing the motion of ions through the solution is estimated by the equation due to Onsager (1926, 1927).

$$\text{Relaxation force} = \frac{e^3 Z_i \kappa \omega \psi}{6 \epsilon k T} \quad (1-4)$$

where  $\psi$  is the applied potential gradient;  $\omega$  and  $g$  are defined by

$$\omega = Z_+ Z_- \frac{2g}{1+g^2}, \quad g = \frac{Z_+ Z_-}{Z_+ + Z_-} \cdot \frac{\lambda_+ + \lambda_-}{Z_+ \lambda_- + Z_- \lambda_+} \quad (1-5)$$

and  $\lambda$  is the ionic conductance of the respective ions.

The movement of the ionic atmosphere along with the associated solvent molecules in the opposite direction to the central ion causes a viscous drag on the ion known as the electrophoretic effect. Assuming the applicability of Stoke's law, Debye and Huckel (1923, 1924) derived the



following expression for the electrophoretic force on the ion

$$\text{electrophoretic force} = \frac{eZ_i \kappa K_i \psi}{6\pi\eta} \quad (1-6)$$

where  $K_i$  is the coefficient of frictional resistance of the solvent opposing the motion of the ion,  $\eta$  is the viscosity of the solvent and the other items are defined as before.

In diffusion each ion of the diffusing electrolyte can be regarded as moving under the influence of two forces (a) the gradient of the chemical potential for that ionic species and (b) an electrical field produced by the motion of oppositely charged ions. The more mobile ions will tend to diffuse faster than the less mobile ones, and by doing so, will create on a microscopic scale a charge separation or a gradient of electrical potential in solution. This will have the effect of increasing the speed of the slower ions and of decreasing the speed of the faster ions. The resultant speed of both ions must ultimately be equal since it is an experimental fact that a macroscopic charge separation is not possible (Robinson and Stokes, 1959).

#### 4. Diffusion coefficients and their interpretation in porous media

Self-diffusion, where radioisotopes are used to follow the diffusion, is the simplest kind of diffusion since the chemical gradient does not exist here and all that occurs is the replacement of nonradioactive ions by radioactive ions. The solvent displacement is negligible so that the effect of electrophoresis vanishes. On the other hand, since positive and negative ions move relative to one another, the time of relaxation effect is an important factor in self-diffusion.



The quantitative measurement of the rate at which a diffusion process occurs is usually expressed in terms of the diffusion coefficient as defined by Fick's First Law.

$$dQ = -DA \frac{dc}{dx} dt \quad (1-7)$$

where  $dQ$  represents the amount of material diffusing in time  $dt$  during which all conditions may be considered to remain constant across a plane of area  $A$  at right angles to the direction of diffusion. The concentration gradient at the plane is  $dc/dx$ .  $D$  has the dimensions of  $\text{length}^2/\text{time}$  and represents the amount of material that in unit time and with unit concentration gradient would cross a plane of unit area at right angles to the direction of diffusion. An alternate form in which Fick's law is expressed is

$$J = -D \frac{dc}{dx} \quad (1-7a)$$

where  $J$  is the flux, i. e. the amount diffusing per unit time per unit cross-section perpendicular to the direction of diffusion.

The treatment of diffusion in porous media is usually based on the model of a single homogeneous phase or a two phase system. "The effective diffusion coefficient in any porous medium is a macroscopic average over a large number of ions in pores of different sizes, shapes and directions, and at larger and smaller distances from the pore walls, expressing the average ability of the species to make headway in any given direction. The quasi-homogeneous treatment which uses such a coefficient is consistent if and only if all possible kinds of self-diffusion







processes can be described in terms of one unique coefficient. Thus the retarding effect of the matrix for a given ionic species must always be the same regardless of the particular nature of the diffusion process" (Helfferich, 1962).

The reduction in the diffusion coefficient of the ionic species in porous media is due to (1) reduction in the area available for diffusion, (2) tortuous path that the ion has to follow, and (3) electrical interactions with the charges of the porous medium if present. The ratio of  $\frac{\bar{D}_i}{D_i}$  where  $\bar{D}_i$  is the diffusion coefficient of the species through the porous medium and  $D_i$  is that in solution, is a useful index of the overall retardation brought about by the porous material.

Helfferich has summarized as follows the various models that are currently used by various workers. Among the most widely used are the treatments due to Wheeler (1951) and Mackie (1955). Their equations are as follows:

$$\bar{D}_i = \frac{D_i \epsilon}{2} \quad (\text{Wheeler}) \quad (1-8)$$

$$\bar{D}_i = \frac{D_i \epsilon^2}{2 - \epsilon} \quad (\text{Mackie}) \quad (1-9)$$

where  $\epsilon$  is the fractional pore volume. Mackie's relation differs from Wheeler's in that his model leads to an increase in tortuosity of the diffusion path with decreasing fractional pore volume.

Prager (1961) has treated diffusion on a statistical basis. His treatment in spite of being considerably more elaborate makes use of a model that resembles Wheeler's.



All of these approaches neglect the electrical interactions of the ions with the exchange resin and purport to explain the reduction in their diffusion coefficient on the basis of reduction in the area through which the ions can migrate and their tortuous path. Thus  $\frac{\epsilon}{2}$  and  $\frac{\epsilon^2}{2-\epsilon}$  are merely geometrical tortuosity factors.

Penman (1940) studied the diffusion of gas through porous media. He suggested that  $\bar{D}_i/D_i = (2/3)\epsilon$ . Bell and Grosberg (1961) have made use of Maxwell's (1873) expression for conduction through a continuum of good conductor with spheres of insulator interspersed in the conductor.

$$K = K_s \left( \frac{1 - \left\{ 1 - \frac{aK_s}{K_p} \right\} b}{1 + (a - 1) b} \right) \quad (1-10)$$

$$\text{where } a = \frac{3K_s}{2K_s + K_p}, \quad b = \frac{V_p}{V_s + V_p}$$

$K_s$  is the conductivity of the conductor,  $K_p$  is the conductivity of the pores, the spherical air spaces in the good conductor, and  $V_p$  and  $V_s$  are the relative volumes of pore and solid. For the case of diffusion the suffixes must be interchanged i. e. the interspersed spheres are the solid. Thus  $b = (1-\epsilon)$ . Assuming the diffusion of solid is zero we get  $\bar{D}_i/D_i = 2\epsilon/3-\epsilon$ . For small values of  $\epsilon$ , we get Penman's expression. Maxwell's equation applies strictly to materials with high porosity. Nevertheless it shows good agreement with low porosities for packings of glass spheres and sand.

As pointed out earlier, most of the models regard the reduction in the diffusion of the species as being due to steric hindrances disregard-



ing ionic interaction with the exchanger. Boyd (1947) however has shown some awareness of this fact, in his equation

$$\bar{D}_i = \frac{D_i}{\lambda_i} \quad (1-11)$$

where  $\lambda_i$  the molar distribution coefficient is equal to the ratio  $\bar{C}_i$  the concentration in exchanger phase and  $C_i$ , that in solution phase. In spite of this "none of the theoretical relations which have so far been developed is entirely satisfactory. Reliable predictions of diffusion coefficients in ion exchanger would require more information and much more elaborate models" (Helfferich, 1962).

#### 5. The mechanism of diffusion in soil

As opposed to most of the treatments for diffusion in ion-exchange resins, which have considered the retardation in the diffusion of a species as predominantly a geometrical effect, the workers in the field of soil colloidal chemistry have recognized the importance of the interaction of the ionic species with the charged surfaces. This is necessary when one considers the essential difference between the common exchange resins and the clay colloids in relation to the ambient adsorbed species as explained earlier.

After Husted and Low (1954) Bloksma (1957) was amongst the earlier workers to study diffusion in clay systems. He measured diffusion coefficients of sodium and iodide ions and urea in clay suspensions. His treatment of diffusion in pure clay systems is as follows.

If  $W_i$  is the mobility of ion  $i$  defined as the velocity under the





influence of an external force of 1 dyne then

$$D_i = kTW_i \quad (1-12)$$

where  $D_i$  is the diffusion coefficient of ion  $i$  and  $k$  and  $T$  are as defined before. In clay suspensions diffusion is affected by adsorption and by the geometry of the diffusion path. Allowance is made for the geometry of the diffusion path by adding a "labyrinth factor"  $h$  to the right hand side of Equ. 1-12.

$$\bar{D}_i = kTW_i h \quad (1-13)$$

The value of  $h$  was considered to be the mean of the square of the cosine of the angle between the average path followed in diffusion and the direction of overall diffusion. Since iodide ions and urea molecules are not adsorbed the reduction in their diffusion coefficients must have been due to the labyrinth factor alone. In the case of adsorbed ions, Bloksma took the concentration of ions adsorbed on the clay as ' $s$ ' per  $\text{cm}^3$  of paste, that of the unadsorbed ions as ' $n$ ' per  $\text{cm}^3$ , and assigned to all the adsorbed ions labyrinth factor ' $g$ ' while those not adsorbed were assigned a labyrinth factor ' $h$ '. Since ion-exchange is a fast process compared with diffusion, all the sodium ions during the fraction of time  $\frac{s}{n+s}$  will have the properties of adsorbed ions and consequently the labyrinth factor  $g$ . During the remainder of the time they will have the labyrinth factor  $h$  equal to that of the iodide ions. Thus Equ. 1-13 becomes

$$\bar{D}_i = kTW_i \left[ g \left( \frac{s}{n+s} \right) + h \left( \frac{n}{n+s} \right) \right] \quad (1-14)$$

Bloksma obtained the value of  $h$  from iodide and urea diffusion and by assuming the same  $h$  to hold for the diffusion of sodium obtained the value



of  $g$  from the experimental self-diffusion coefficient. The limiting value as obtained from the Nernst equation was used for  $kTW_i$  in the above expression. The equivalence of  $h$  obtained from urea and iodide diffusion verified the assumption of nonadsorbability of the iodide ion. Having no charge, the urea molecule can not be adsorbed.

Porter et al, (1960) treated diffusion in soil as follows. In soil the effective fraction of the total area available for flow is not the pore fraction  $\epsilon$  but is  $\epsilon(L/Le)$  where  $L$  is the macroscopic distance between two points and  $Le$  is the actual distance through which the diffusion must take place. As the actual distance  $Le$  through which an ion is constrained to travel is always greater than the macroscopic distance  $L$  in the direction of diffusion,  $dx$  in Equ. 1-7 must be greater by a factor  $Le/L$ . Interactions between the diffusing ions and the ions associated with the charged mineral particles act to decrease the diffusivity. A factor  $\gamma$  was used to account for this effect. Thus Equ. 1-7 becomes

$$\frac{dQ}{dt} = \bar{D} \gamma \left(\frac{L}{Le}\right)^2 A \frac{dc}{dx} \quad 1-15$$

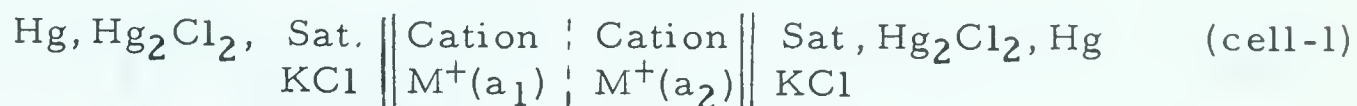
As can be seen the factor  $(L/Le)^2$  and  $h$  from Bloksma's treatment are equivalent. Thus the effective diffusion coefficient

$$\bar{D}_i = D_o \gamma h \quad 1-16$$

$D_o$  is the diffusion coefficient in pure solution. Fletcher and Slabaugh (1960) and Gast (1962) determined the self-diffusion coefficients for different cations with a similar setup as used by Bloksma. Assuming the value of  $h$  obtained by Fletcher and Slabaugh for 9% and 10% clay suspensions, Gast determined the values of  $\gamma$  for different cations from his



self-diffusion coefficients. He found that these values were of similar magnitude to those of "fraction active" as found by Marshall (1951). Fraction active as defined by Marshall corresponds to the activity coefficient in electrochemistry and was determined from the concentration cell.



Where  $\left\| \begin{array}{c} \text{Cation} \\ \text{M}^+(\text{a}_1) \end{array} \right\| \begin{array}{c} \text{Cation} \\ \text{M}^+(\text{a}_2) \end{array} \left\|$  is the clay membrane electrode reversible with respect to the particular cation in question. The potential of this cell is given by the Nernst equation

$$E = -\frac{RT}{F} \ln\left(\frac{a_2}{a_1}\right) \quad (1-17)$$

A standard solution of known activity was placed on one side, and the activity of the homoionic clay suspension on the other side of the clay membrane electrode was calculated from the measured electrode potential  $E$ . Knowing the concentration of the ions in the clay suspension, one can determine the fraction active.

The present treatment of diffusion in soil is intended to throw some light on the parameter  $\gamma$  with regard to its equivalence to the fraction active as defined by Marshall. The fundamental flow equation (Spiegler, 1956) for ions states that the flux of the ionic species  $i$ ,  $J_i$ , in the  $x$  direction is proportional to their molar concentration  $c_i$  and to the sum of all the forces that tend to move them. If the force present is a diffusive one, the constant of proportionality  $U_i$  is called the diffusion mobility and has the units of  $\text{mole cm.}^2 \text{sec.}^{-1} \text{joule}^{-1}$ .





$$J_i = -U_i c_i \frac{d\mu}{dx} \quad (1-18)$$

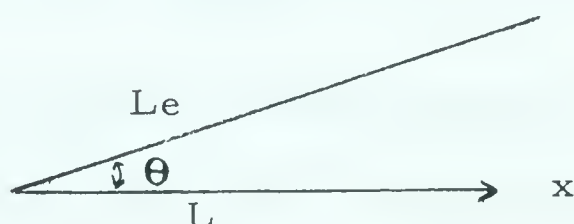
where  $d\mu/dx$  is the gradient of chemical potential. Since  $d\mu = RT \ln a$  we have

$$\begin{aligned} J_i &= -\frac{(U_i c_i RT)}{a_i} \frac{da_i}{dx} = -\left(\frac{U_i c_i RT}{a_i} \frac{da_i}{dc_i}\right) \frac{dc_i}{dx} \\ &= -\left(U_i RT \frac{d \ln a_i}{d \ln c_i}\right) \frac{dc_i}{dx} \end{aligned} \quad (1-19)$$

Comparing Equ. 1-7a and 1-19 we see that

$$D = \left(U_i RT \frac{d \ln a_i}{d \ln c_i}\right) \quad (1-20)$$

In the soil consider the situation where the diffusion is being measured in the x direction. Due to the presence of soil particles and complex pore geometry, the ions are constrained to take the path Le



instead of L. If the force in the x direction in an aqueous solution (without solid matrix) is  $d\mu/dx$ , then the force along Le, the path followed in soil, would be  $d\mu/dx \cos \theta$  and the flux along Le would be

$$J_i \rightarrow Le = -\epsilon U_i c_i \frac{d\mu}{dx} \cos \theta \quad (1-21)$$

Here the pore fraction  $\epsilon$  takes into account the fact that the area available for diffusion is  $\epsilon A$ . Since the diffusion is being measured in the x direction the component of  $J_i$  in the x direction would be

$$J_i = -\epsilon U_i c_i \frac{d\mu}{dx} \cos^2 \theta \quad (1-22)$$



Equation 1-22 is based on the similar treatment by Mackie (1955). On comparing Equ. 1-18, 1-19 and 1-22 we get

$$J_i = - \left( \epsilon U_i R T \cos^2 \theta \frac{d \ln \bar{a}_i}{d \ln c_i} \right) \frac{dc_i}{dx} \quad (1-23)$$

Comparing Equ. 1-23 with 1-7a we again see that

$$\bar{D}_i = + \left( \epsilon U_i R T \cos^2 \theta \frac{d \ln \bar{a}_i}{d \ln c_i} \right) \quad (1-24)$$

From Equ. 1-20 one can see that for an infinitely dilute solution

$$\frac{d \ln \bar{a}_i}{d \ln c_i} = 1 \text{ and}$$

$$D_o = U_i R T \quad (1-25)$$

Equation 1-25 is the Nernst-Einstein equation. Substituting Equ. 1-25 into 1-24 we get

$$\bar{D}_i = D_o \epsilon \cos^2 \theta \frac{d \ln \bar{a}_i}{d \ln c_i} \quad (1-26)$$

Equation 1-26 is an important result from the point of view of this study and will be referred to frequently. It can be seen that  $\cos^2 \theta$  corresponds to Porter's  $(L/Le)^2$  and Bloksma's  $h$ . However, it is believed that the factor  $d \ln \bar{a}_i / d \ln c_i$  corresponds to  $\gamma$  which is shown in the above treatment for the first time. This factor would approach 1 as the ions approach their ideal behavior, since the activity and the concentration of the ionic species would become identical, the activity coefficient being close to 1. Since this work was completed Low and Dutt (1964) have derived a relation similar to Equ. 1-26.

The diffusion mobility  $U_i$  (mole cm.<sup>2</sup> wattsec.<sup>-1</sup> sec.<sup>-1</sup>) is related to the electrical mobility  $u_i$  (cm.<sup>2</sup> volt<sup>-1</sup> sec.<sup>-1</sup>) and the absolute mobility  $W_i$  (cm.<sup>2</sup> sec.<sup>-1</sup> dyne<sup>-1</sup>) by



$$U_i = \frac{u_i}{zF} = \frac{W_i}{N} \quad (1-27)$$

where F is a Faraday i. e. 96,500 coulombs and N is Avogadro's number.

The specific conductance  $K_{sp}$  is the current flowing in a conductor of unit cross-section under unit potential gradient. The total ionic charge in a unit volume is  $Fc$ , if  $c$  is measured in equivalents per unit volume.

This total ionic charge moving with velocity  $u_i$  constitutes  $K_{sp}$ .

$$K_{sp} = Fcu_i \quad (1-28)$$

However, in specific conductance both the cations and anions make positive contributions to  $K_{sp}$  even though their velocity vectors have opposite signs. Thus the total charge of species  $i$  moving with velocity  $u_i$  would constitute  $t_i K_{sp}$  where  $t_i$  is the fraction of the total current carried by species  $i$  and is called the transport number. Hence

$$t_i K_{sp} = Fcu_i \quad (1-29)$$

From Equ. 1-25 and 1-27 we also have

$$D = \frac{u_i RT}{zF}$$

or 
$$u_i = \frac{DzF}{RT} \quad (1-30)$$

Then from Equ. 1-29 and 1-30 we have the relation

$$u_i = \frac{t_i K_{sp}}{Fc} = \frac{DzF}{RT} \quad (1-31)$$

which is nothing but the Nernst-Einstein relation equating the diffusion and electrical mobility of the ions. Since both diffusion and electrical conductance in electrolytic solutions involve the motion of ions, it is therefore to be expected that a relation will exist between the diffusion





coefficient of an electrolyte and its equivalent conductance. The most important differences between the two processes are

(a) in conduction positive and negative ions move in opposite directions, while in diffusion they move in the same direction,

(b) in conduction, at the limit of extreme dilution, the various ions of the electrolyte move independently of each other; whereas in diffusion they are obliged to move at equal speeds since otherwise a separation of charge would occur.

Both processes can be regarded as being derived from small perturbations of the ordinary molecular motions; in diffusion it is the concentration gradient and in conduction it is the external field reinforced or opposed by the concentration gradient.

The Nernst-Einstein equation holds if the mechanism underlying diffusion is the same as that responsible for electrolytic conductance. In electrolytic solutions the Nernst-Einstein relation holds strictly only at infinite dilution. At finite concentrations, the diffusion and electrical mobilities are not the same because the interactions between the cation and anions are different in the two processes.

To complete the above treatment electrical conductance in the soil will now be considered. Introducing the electrical force in Equ. 1-18 instead of the generalized diffusive force and using the earlier analogous argument we get

$$J_i = - \epsilon U_i c_i \cos^2 \theta \left( z F \frac{d\psi}{dx} \right) \quad (1-32)$$



For unit electrical potential with  $U_i = u_i/zF$  we get

$$J_i = \epsilon u_i c_i \cos^2 \theta \quad (1-33)$$

where  $J_i$  is the flux per unit area per second. With the argument implicit in Equ. 1-28 and 1-29 we have

$$t_i K_{sp} = \frac{\epsilon F u_i c_i \cos^2 \theta}{10^3} \quad (1-34)$$

Comparing Equ. 1-34 and 1-24 we have the Nernst-Einstein relation as applicable to soil

$$\frac{t_i K_{sp} 10^3}{\epsilon F c_i (\cos^2 \theta)} = \frac{DzF}{RT \cos^2 \theta \epsilon \left( \frac{d \ln \bar{a}}{d \ln c} \right)} = u_i \quad (1-35)$$

In soil the flow of ions takes place through the pores which are joined together in a random fashion forming a channel. The electrical conduction here could take place in the parallel or the series array. In the parallel array the flow of charge passes through the different channels along parallel lines and the total resultant flow is composed of the sum of the contributions from different pore channels. In the series array in which the same flow passes through all the channels, the partial flow through these equals the resultant charge flow (Kedem and Katchalsky, 1963).

In the above treatment no assumption has been made regarding the contribution of microconductors in the form of continuum of pores to the specific conductance of the soil system.

## 6. Soil as a permselective material and theory of membrane potential

Letey and Klute (1960) have made use of the Nernst-Einstein relation and determined the apparent mobilities of potassium and chloride



ions in soil and clay paste. In the study of ion-migration the importance of the geometry of the ionic path cannot be overemphasized. The study with pure clay systems will undoubtedly throw some light on the relationship of clay surfaces and the ions associated with them. However, the geometry of the ionic path through these systems is completely different from that of soil systems so that the findings can only be applied to soil in a restricted way. The use of soil for such a study was a step in the right direction, however, Letey and Klute did not determine the geometry factor but combined it with the mobility which they called the apparent mobility. Thus their Nernst-Einstein relation reads

$$\frac{10^3 t_i K_{sp}}{z_i F c_i} = \frac{D z_i F}{R T} = u \text{ (apparent)} \quad (1-36)$$

The above workers determined the transference numbers by the Hittorf method (1960). They inserted the soil plug into the central chamber with the assumption that there is no change in the concentration of solution in the plug. Then they proceeded to point out the various errors that are likely to be caused by such an assumption. In short these errors are:

- (1) since the transference number of the cation in the soil is greater than in the solution within the plug, there would be zones of accumulation and depletion on the sides of the cathode and the anode, respectively, which violates the basic assumption;
- (2) resultant diffusion;
- (3) accumulated salts and depleted solution in the porous





plug which are not analyzed.

(4) water transport by electro-osmosis;

(5) hydrolysis in the zone of depletion.

Soils belong to the class of permselective materials since they transfer certain types of ions, namely cations, in preference to others i. e. anions. Membranes or plugs containing ion exchange resins and clays are permselective. The basic observation in the electrochemistry of permselective materials refers to their electromotive action which becomes conspicuous when it separates two electrolytic solutions which are not identical in concentration. The electromotive force that arises in such a case is different from the liquid junction potential which would arise between the same two solutions in the absence of permselective materials. The electromotive force arising is termed the membrane potential or the plug potential depending on whether a membrane made of permselective material or a plug is interposed.

The electromotive action of a permselective material depends on the degree to which it affects the behavior of cations or anions during their passage through it. All permselective materials have a fixed charge, either positive for anion exchangers or negative for cation exchangers, depending on which they adsorb the mobile anions or cations. The closer the fixed charge groups, i. e. the smaller the pores the greater the electrical field until it virtually excludes co-ions. Since membranes have smaller pores, they have higher effective electrical charge and virtually prevent the transfer of ions having the same



charge as that of the membrane, i.e., co-ions. With membranes of very low porosity the membrane potential may reach the magnitude of the potential difference which would arise between the two solutions if they were connected to each other through a pair of reversible electrodes, specific either for the cations or the anions in solution. This thermodynamically possible maximum value of the potential represents the upper limit of possible membrane concentration potentials; the liquid junction potential being the other limit. The membrane is considered ideal when the transport number of the counterion is one and when the upper limit of potential is reached.

All ion exchange membranes lose permselectivity with increasing concentration of the solution which they separate. This loss is due to increasing penetration of co-ions and also due to electro-osmosis which reduces the specific influence of the membrane. The loss of permselectivity is often termed ion leakage.

In porous plugs of permselective material or in defective membranes a leak due to the continuous connection between the two solutions through the liquid phase in the pores occurs. If the specific conductance of the ion exchanger is high and the solutions are very dilute, this leak does not affect the membrane potential appreciably. But when the larger proportion of the ion transport takes place through the conductive liquid phase of the pores, the effect of the leak overshadows the specific effect of the ion exchange material. Thus porous plugs of many ion exchangers would behave almost as a perfect membrane when



they separate very dilute solutions. On the contrary, if the solutions are concentrated the solid acts as if it were an inert material and the potential difference between the two solutions approaches the liquid junction potential, the lower limit as mentioned earlier. (Spiegler et al., 1956)

Soil materials generally have much lower exchange capacity or charge than the many exchange resins and membranes prepared from them. However, it is the hypothesis of the present study that a range of concentrations of the electrolyte exists during which a soil plug will display almost perfect membrane potentials. In this range of concentration many of the existing theories of membrane potential would, it is contended, become applicable to soil plugs even though they are a far cry from the rigid, homogeneous membranes that are conventionally used. A soil plug would be a heteroporous medium with a mosaic of wider and narrower channels. Thus the electrical interactions between the ions and the charges on the particle surfaces forming the walls of the channels will be heterogeneous and the observable plug potentials would be the gross result of the interactions within the pores.

The current theories of membrane systems can be classified into three more or less distinct groups (Schlogl, 1956).

The theories of the first group consider the membrane as a surface of discontinuity separating the two adjacent phases and setting up different resistances to the passage of the various molecular and ionic species. The driving force for particle transfer across the membrane is the difference in the general chemical potential between the







two adjacent phases (Mazur and Overbeek, 1951; Overbeek, 1953; Staverman, 1952; Wiebenga, 1946).

The theories of the second group consider the membrane as a quasi-homogeneous intermediate phase of finite thickness. Here the driving forces are the local gradients of the general chemical potentials in the layer. Convection may also contribute to particle transfer within the membrane (Erikson, 1949, 1950; Goldman, 1943; Hodgkin and Katz, 1949; Keynes, 1951; Kirkwood, 1954; Kobatake, 1955, 1956; Lorenz, 1952; Mackie and Meares, 1956; Meares and Ussing, 1959; Meyer and Sievers, 1936; Scatchard, 1953; Schlogl, 1954; Schlogl and Schodel, 1955; Schmid, 1950; Spiegler, 1958; Teorell, 1935.).

The theories of the third group consider the membrane as a series of potential energy barriers. Thus the membrane is an inhomogeneous intermediate layer. An irregular spatial lattice is formed because the probability of finding a particle is higher in the positions between the activation thresholds. The driving force arises from the differences between the transition probabilities in opposite directions normal to the membrane (Daveson and Danielli, 1943; Laidler and Schuler, 1949; Zwolinski et al., 1949). When the number of activation thresholds becomes very large and the distance between the lattice points sufficiently small (a situation usually found in ion exchangers) these theories give the same results as those of the second group.

The theories of the first group have the advantage of being relatively simple. For ion-exchanger membranes, however, they are often

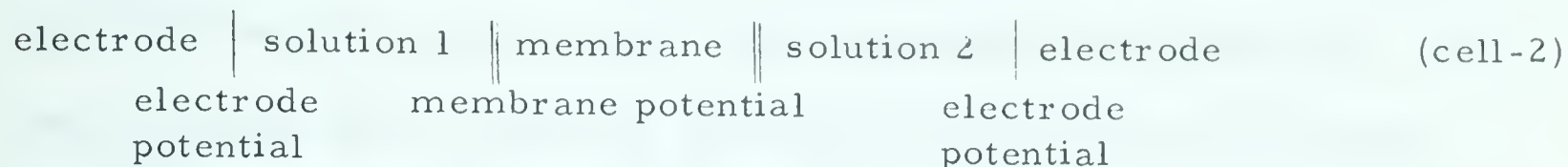


inadequate. The thermodynamics of irreversible processes (Groot, 1951) have often been used to describe membrane phenomena along the lines of either the first or the second group theories (Kirkwood, 1954; Kobatake, 1955; Lorenz, 1952; Lorimer et al., 1956; Mackey and Meares, 1959; Mazur and Overbeek, 1951; Overbeek, 1953; Spiegler, 1958; Staverman, 1952; Wiebenga, 1946). Such treatments are still quite general and only the physical interpretation of the coefficients in them requires the use of a model. These theories, however, are still in an early stage of their development. A general unified treatment including systems with concentration gradients in the membrane, allowing for the concentration dependence of the various coefficients, has not yet been achieved. In one of the later chapters the use of thermodynamics of irreversible processes for transport processes in soil will be dealt with when the existing theories and different treatments will be elaborated.

The leading theory of permselective membranes is due to Teorell (1935) and Meyer and Sievers (1936) who postulated it independently. The membrane is considered as an isotropic porous diaphragm with an even distribution of charges throughout. Consider a membrane interposed between solutions of an electrolyte of differing concentration. The essential feature of the Teorell-Meyer and Sievers theory is that there exists a permanent and instantaneous Donnan equilibria between the solution and the interfaces of the membrane. This gives rise to two Donnan potentials due to unequal charge distribution in the boundary zone. These potentials along with the diffusion potential in the interior of the



membrane give rise to the membrane potential. The membrane potential itself cannot be measured directly. Any electromotive measurement can only give the electromotive force (e.m.f.) of the whole cell.



In order to obtain the membrane potential from the e.m.f., assumptions about the electrode potentials, which are also single potential differences must be made.

A standard procedure in electrochemistry is the use of calomel electrodes in potential measurements.



Usually it is assumed that the electrode potentials of the calomel electrodes balance one another exactly so that the membrane potential and the e.m.f. of the cell are equal. It can be shown that this assumption is equivalent to a definition of single-ion activity coefficient. A considerable controversy has arisen in the field of colloid chemistry on the basis of such an assumption when the solutions contain polyvalent ions or poly-electrolytes. This aspect will be dealt with again in connection with the diffusion in soil systems.

The diffusion potentials at the KCl bridges -- "problem children of electrochemistry" (Helfferich, 1962) -- can be avoided by the use of reversible electrodes which are inserted directly into the solution. For example









The electrodes are reversible with respect to the  $\text{Cl}^-$  ions present in both solutions. The potential of a reversible electrode is a function of the activities of the ions involved. Since solutions 1 and 2 differ in concentration, the two electrode potentials are not equal and the membrane potentials differ from the emf. measured. However, the theoretical expression for the the emf. of this cell involves only mean activities which are thermodynamically well-defined. Fig. 1 illustrates the difference between an uncharged membrane from that of a charged one in the distribution of electrolyte (Teorell, 1953). Note that in spite of the identical bulk concentration differences ( $a_1 - a_2$ ) the concentration gradient within the charged membrane is greater.

According to the Nernst-Planck equation the flux of the ionic species under ideal conditions is given by

$$J_i = (J_i)_{\text{diff.}} + (J_i)_{\text{elec.}} = -U_i \left( \text{grad } c_i + z_i \frac{c_i F}{RT} \text{grad } \psi \right) \quad (1-37)$$

It should be emphasized that the total force causing the flux of an ion can be composed of not only concentration (activity) gradients but may also include superimposed forces originating from an electrical potential, hydrostatic-osmotic pressure gradients etc. Fig. 2 illustrates these forces in a membrane system. Note that  $dc_i/dx$  and  $d\psi/dx$  have opposite signs. Since  $dc_i/dx$  is negative, the diffusive force  $-\frac{RT}{c_i} \frac{dc_i}{dx}$  is positive. Similarly since  $d\psi/dx$  is positive, the electrical force  $(-zF d\psi/dx)$  is negative. Thus the electrical force opposes the movement of cations and accelerates that of anions since the valence  $z$  would have negative sign



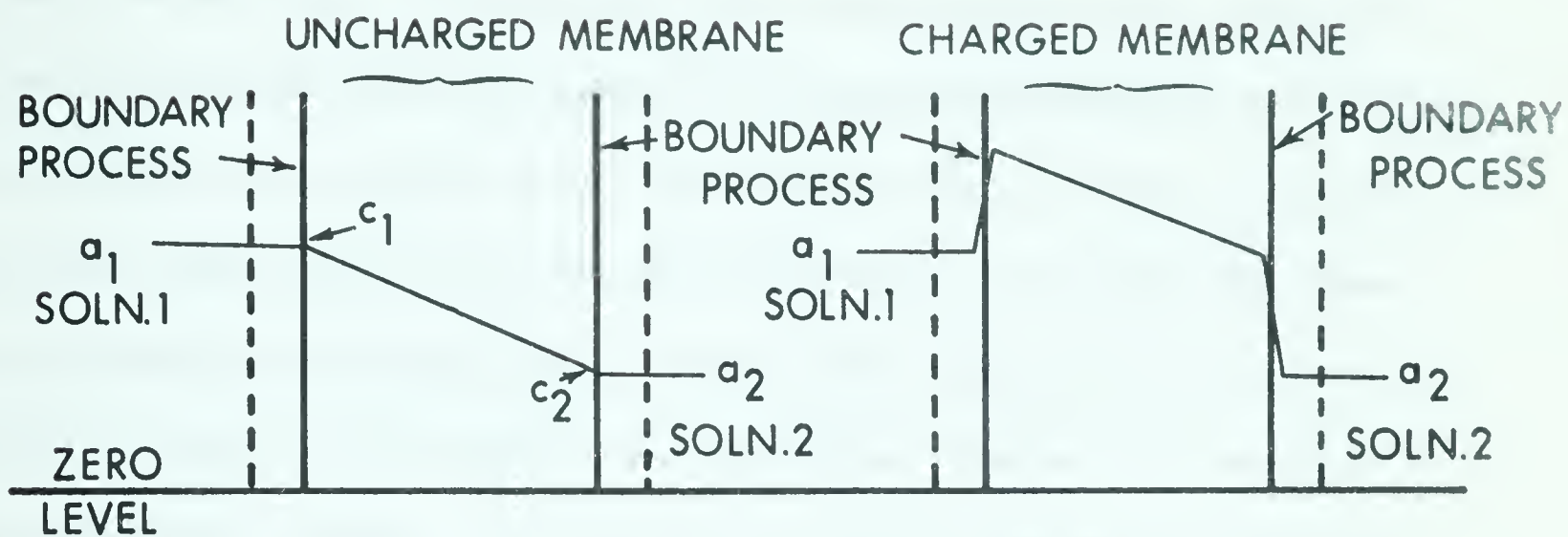


FIG.1 CONCENTRATION GRADIENT WITHIN A CHARGED AND UNCHARGED MEMBRANE

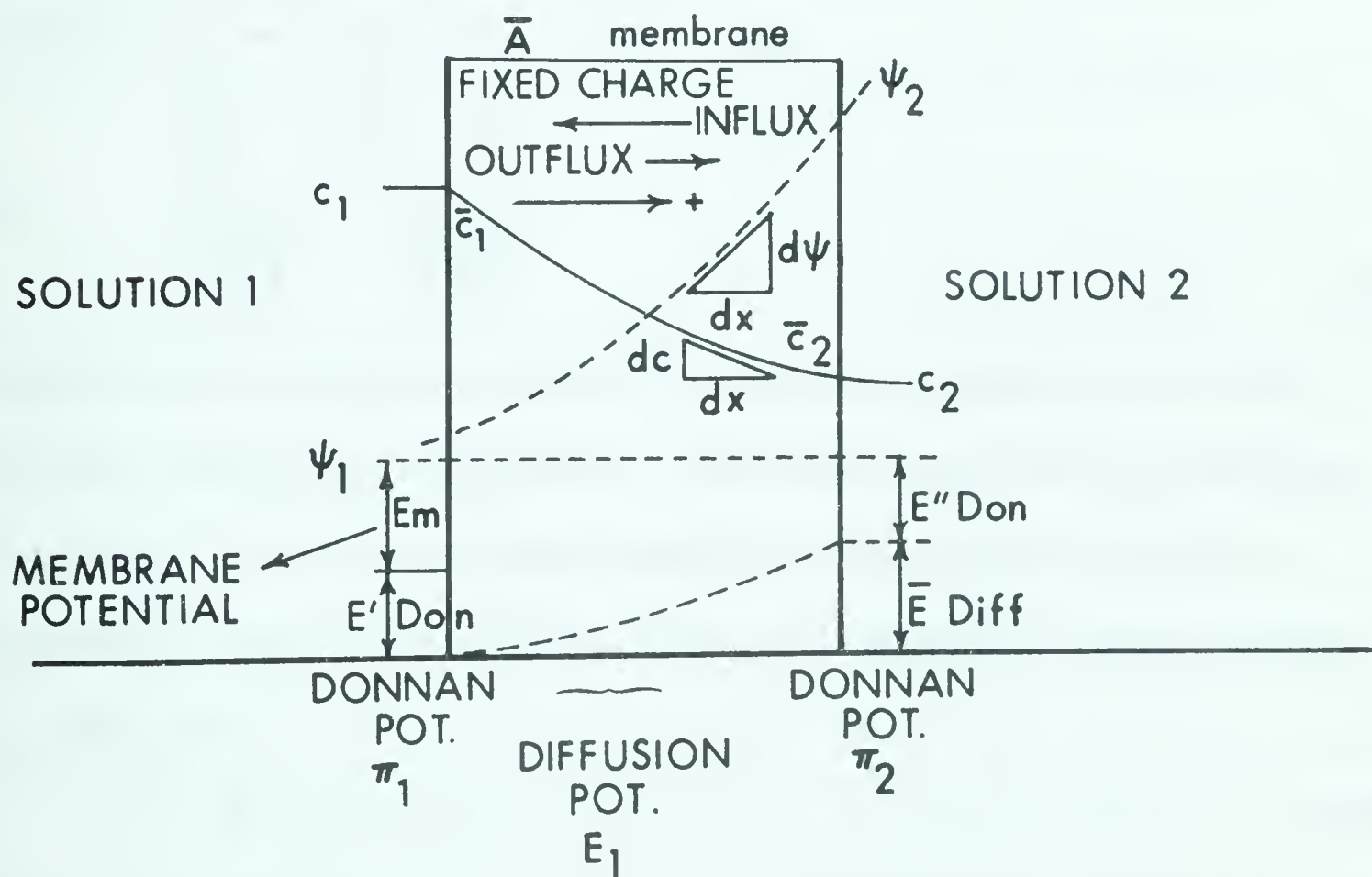


FIG.2 CONCENTRATION AND POTENTIAL GRADIENTS WITHIN THE MEMBRANE AND DECOMPOSITION OF MEMBRANE POTENTIAL



here. The value for  $\bar{A}$  gives the concentration of the counterion in gm. equivalent per kgm.  $H_2O$  adsorbed on the fixed charges of the membrane. It is assumed that the fixed charge  $\bar{A}$  is constant and that there is complete dissociation of the counter-ions. This concentration of fixed charges is the most fundamental parameter of the membrane. Provided that there are no large or uncharged pores through which electrolyte can leak, it will determine the selectivity of the membrane. Hence, it is known as the selectivity constant. Knowing the selectivity constant the concentration of the ions within the membrane is calculated by Donnan equilibrium (Hills, 1961). Designating  $i$  for counter-ions and  $j$  for co-ions, the condition of electroneutrality requires that

$$\begin{aligned} & \left[ \bar{A} + \bar{m}_j \right] = \bar{m}_i \\ \text{and} \quad & \left( \frac{\bar{a}_i}{\bar{\gamma}_i} \right) = \bar{A} + \left( \frac{\bar{a}_j}{\bar{\gamma}_j} \right) \end{aligned} \tag{1-38}$$

where the concentrations of diffusible species are expressed in molal activities and activity coefficients. The barred terms refer to the membrane phase. At thermodynamic equilibrium, the partial molal free energies of  $i$  and  $j$  in the outside solution and inside the membrane would be equal so that

$$\bar{a}_i, \bar{a}_j = a_i, a_j \tag{1-39}$$

Making use of Equ. 1-38

$$\left( \frac{\bar{a}_i}{\bar{\gamma}_i} \right) = \bar{A} + \left( \frac{a_i \cdot a_j}{\bar{a}_i \cdot \bar{\gamma}_j} \right) \tag{1-40}$$

This leads to





$$\left(\frac{\bar{a}_i}{\bar{\gamma}_i}\right)^2 = \frac{\bar{A} \cdot \bar{a}_i}{\bar{\gamma}_i} + \frac{a_i \cdot a_j}{\bar{\gamma}_i \cdot \bar{\gamma}_j} \quad (1-41)$$

which can be solved as a quadratic with  $\bar{m}_i = \bar{a}_i / \bar{\gamma}_i$  to yield

$$\bar{m}_i = \frac{\bar{A}}{2} + \left[ \frac{\bar{A}^2}{2} + \frac{m_{\pm}^2 \gamma_{\pm}^2}{\bar{\gamma}_{\pm}^2} \right]^{\frac{1}{2}} \quad (1-42)$$

and

$$\bar{m}_j = -\frac{\bar{A}}{2} + \left[ \frac{\bar{A}^2}{2} + \frac{m_{\pm}^2 \gamma_{\pm}^2}{\bar{\gamma}_{\pm}^2} \right]^{\frac{1}{2}} \quad (1-42)$$

where  $m_{\pm} \gamma_{\pm}$  represents the mean molal activity  $a_{\pm}$  of a uni-univalent electrolyte, ij, in equilibrium with the membrane and  $\gamma_{\pm}$  is the mean molal ionic activity coefficient inside the membrane phase. From Equ. 1-42 it can be seen that for small values of  $\frac{m_{\pm} \gamma_{\pm}}{\bar{A} \bar{\gamma}_{\pm}}$ ,  $\bar{m}_i \rightarrow \bar{A}$  and  $\bar{m}_j \rightarrow 0$ .

The unequal distribution of diffusible ions at the interface is accompanied by a potential difference called the Donnan potential, given by

$$\Pi = \frac{RT}{z_i F} \ln \frac{a_i}{\bar{a}_i} \quad (1-43)$$

These phase boundary potentials are not accessible to measurements by electrodes reversible with respect to a particular ion. They are normally measured by the use of calomel electrodes connected by means of a salt bridge, with the tacit assumption of negligible liquid junctions. Since the membrane separates two solutions of different composition, there are two unequal Donnan potentials, corresponding to the two interfaces, which together with the intramembrane diffusion potential give rise to volta



potentials which are measurable.

The sum of the two Donnan potentials is given by

$$\Pi_1 + \Pi_2 = \frac{RT}{z_i F} \ln \frac{(a_i/\bar{a}_i)_I}{(a_i/\bar{a}_i)_{II}} \quad (1-44)$$

Since  $\bar{a}_i = \bar{m}_i \cdot \bar{\tau}_i$  and  $\bar{m}_i$  is given by Equ. 1-42 and taking into account separate values of  $\bar{A}$ ,  $\bar{\tau}_i$  and  $\bar{\tau}_j$  appropriate to each interface, Hills (1961) gets

$$\Pi_2 + \Pi_1 = \frac{RT}{z_i F} \ln \frac{(a_i)_I}{(a_i)_{II}} \left[ \frac{\bar{A}_{II}^2 (\bar{\tau}_i)_{II}^2 + 4(a_{\pm})_{II}^2 \left( \frac{\bar{\tau}_i}{\bar{\tau}_j} \right)_{II} + \bar{A}_{II} (\bar{\tau}_i)_{II}}{\bar{A}_I^2 (\bar{\tau}_i)_I^2 + 4(a_{\pm})_I^2 \left( \frac{\bar{\tau}_i}{\bar{\tau}_j} \right)_I + \bar{A}_I (\bar{\tau}_i)_I} \right] \quad (1-45)$$

The diffusion potential that arises within the membrane is given by

$$E_j = - \frac{RT}{F} \int_I^{II} \sum \frac{t_i}{Z_i} d \ln \bar{a}_i$$

To integrate the above equation  $\bar{t}_i$ , where the subscript  $i$  is a general one for ionic species  $i$ , must be expressed in terms of  $\bar{a}_i$ . The relationship between  $\bar{t}_i$  and  $\bar{a}_i$  is often complicated. The value of  $\bar{t}_i$  is determined by the irreversible processes of electrical conduction and diffusion. These processes are related to the shape of the ion and the viscosity of the solution. The value of  $\bar{a}_i$  is determined by the chemical potential which is an equilibrium property not related to shape or viscosity in any simple manner. If the solution is dilute one may assume that the ionic activities are equal to  $c_i/z_i$ ,  $c_i$  being the equivalent ionic concentration. The transport numbers are equal to  $c_i u_i / \sum c_i u_i$ , where  $u_i$ , the electrical



mobility, is considered to be independent of the concentration. No integration of the above equation in terms of activities has yet been given, although the difficulties involved have been emphasized by Schlogl and Helfferich (1952). The above simplifying assumptions and also that of linear mixing in the boundary zone are incorporated into a solution of Equ. 1-46 by Henderson (1907, 1908). Another solution by Plank (1890) assumes a constrained boundary. In the original Teorell-Meyer and Sievers theory the Henderson formula was used to estimate the diffusion potential. The Henderson formula requires a linear mixture in every section of the membrane. This is possible when all concentration gradients are linear. The correct treatment would be the one by Plank and it has been incorporated by Teorell (1953).

For uni-univalent electrolytes both the Henderson and Plank solutions lead to identical results.

$$E_j = \frac{RT}{z_i F} \frac{\bar{u}_i - \bar{u}_j}{\bar{u}_i + \bar{u}_j} \ln \left[ \frac{\bar{u}_i(\bar{m}_i)_I + \bar{u}_j(\bar{m}_j)_I}{\bar{u}_i(\bar{m}_i)_{II} + \bar{u}_j(\bar{m}_j)_{II}} \right] \quad (1-47)$$

where  $\bar{u}_i$  and  $\bar{u}_j$  are the mobilities of the counter-ion and co-ion respectively. The total membrane potential is now given by (Hills, 1961)

$$\begin{aligned} E &= \Pi_1 + \Pi_2 + E_j \\ &= \frac{RT}{z_i F} \ln \frac{(a_i)_I}{(a_i)_{II}} \cdot \left[ \frac{\bar{A}_{II}(\bar{\gamma}_i)_{II} \cdot 1 + (1 + \xi^2_{II})}{\bar{A}_I(\bar{\gamma}_i)_I \cdot 1 + (1 + \xi^2_I)} \right] \\ &\quad + \frac{\bar{u}RT}{z_i F} \ln \left[ \frac{\bar{A}_{II} \bar{u} + (1 + \xi^2_{II})}{\bar{A}_I \bar{u} + (1 + \xi^2_I)} \right] \\ \text{where } \bar{u} &= \frac{\bar{u}_i - \bar{u}_j}{\bar{u}_i + \bar{u}_j} \quad \text{and} \quad \xi = 2a_{\pm}(\bar{A} - \bar{\gamma}_{\pm}) \end{aligned}$$





The above theory is based on a number of assumptions which are in practice hardly if ever satisfied. They are: (1) the membrane is a homogeneous phase of constant charge, (2) the mobilities of ions in the membrane are similar to that in the outside solution, (3) the mobility ratio is constant throughout the membrane, and (4) there is no osmotic, hydrostatic or electro-osmotic flow of water.

Due to the above assumptions membranes seldom obey Equ. 1-48. Scatchard (1953) has given a quasi-thermodynamical treatment to a membrane which is regarded wholly as a liquid junction separating two homogeneous solutions. The membrane potential is then given from Equ. 1-46

$$E = -\frac{RT}{F} \int_I^{II} \frac{\bar{t}_i}{z_i} d\ln a_i - \frac{\bar{t}_j}{z_j} d\ln a_j + \bar{t}_w d\ln a_w \quad (1-49)$$

where  $\bar{t}_i$ ,  $\bar{t}_j$  and  $\bar{t}_w$  are transport numbers of the counter-ion, co-ion and the solvent in the membrane phase and  $a_i$ ,  $a_j$  and  $a_w$  are the corresponding activities in the external phase.

Equation 1-49 is an improvement over 1-48 since it indicates the sources of deviation from the permselectivity as expressed by the last two terms on the right hand side. Equation 1-49 also cannot be integrated without the assumptions that are implicit in the derivation of Equ. 1-48. The main assumption of Equ. 1-49 is that there are single values for  $t_i$ ,  $t_j$  and  $t_w$  across the membrane and if this is not so then the average values  $\bar{t}_i$ ,  $\bar{t}_j$  and  $\bar{t}_w$  furnish a good approximation. Thus Equ. 1-49 becomes on



integration

$$E = - \frac{RT}{F} \left[ \frac{\bar{t}_i}{z_i} \ln \frac{(a_i)_{II}}{(a_i)_I} - \frac{\bar{t}_j}{z_j} \ln \frac{(a_j)_{II}}{(a_j)_I} + \bar{t}_w \ln \frac{(a_w)_{II}}{(a_w)_I} \right] \quad (1-50)$$

Eliminating  $a_w$  by the Gibbs - Duhem relation one gets the final equation

$$E = - \frac{RT}{F} \left[ \frac{\bar{t}_i}{z_i} \ln \frac{(a_i)_{II}}{(a_i)_I} - \frac{\bar{t}_j}{z_j} \ln \frac{(a_j)_{II}}{(a_j)_I} - \bar{t}_w \left( 0.018 a_{ij} \ln \frac{(a_i a_j)_{II}}{(a_i a_j)_I} \right) \right] \quad (1-51)$$

where  $\bar{a}_{ij}$  is the average external molal activity.

The average transport numbers are not accessible except by an independent determination by Hittorf transport number, even where, if Letey and Klute's work (op. cit.) is any indication, the errors due to electro-osmotic flow and other analytical difficulties could be many. Thus it must be concluded that none of the existing theories are able to explain unambiguously the behavior of nonideal membranes.

Since soil plugs would necessarily behave as leaky membranes, except perhaps for a range of concentrations, none of the present theories would apply to them completely.

## 7. Objectives of the present study

The objectives of the present study can thus be said to be: (1) To study if being a permselective material, a soil plug, in spite of its very high porous nature in comparison to a true membrane, behaves like an ideal membrane, in a certain range of concentration of electrolytic solutions, (2) Having proved this the next objective is to find the explanation of its non-ideal behavior in other concentration ranges, (3) To investigate the use of the Teorell-Meyer and Sievers theory



qualitatively and quantitatively to explain ion-migration in soil, (4)

Because of numerous assumptions in the present theories, to investigate the use of thermodynamics of irreversible processes, in the phenomenological sense, by making use of the fundamental flux equation (Kirkwood, 1954).

$$J_i = \sum_{j=1}^N L_{ij} X_j \quad (1-52)$$

where  $L_{ij}$  is the permeability matrix of the membrane defined by

$$L_{ij} = \frac{B_{ij}}{R} \quad (1-53)$$

where  $R$  is the determinant of the resistance matrix and  $B_{ij}$  is its appropriate minor, (5) To explain the behavior of the soil plug in its ideal and nonideal range, carry out the electrochemical characterization of the soil and determine, the activity coefficients, the self-diffusion coefficient, transference numbers, conductivity and electro-osmotic flow towards this end, (6) To separate the tortuosity effect from the electrostatic effect on ion-migration in soil and to explain the latter in terms of change in the activity coefficient of the ionic species, (7) To study the above two effects at different stages of dehydration in soil, to find the changes in the magnitude of electrical effects as the ionic species are constrained to move closer to the charges, (8) To determine the activation energies of diffusion for a cation and an anion in soil and correlate them with other results, and (9) To formulate general principles of ion-migration in soil.

## 8. Presentation of results of the study

The bulk of the research carried out under this study can be





roughly grouped under three main topics:

- (1) characterization of the soil system,
- (2) self-diffusion measurements,
- (3) electrochemical measurements.

Research for each of these topics required numerous preliminary experiments before the experiments with the final objective could be carried out. It was decided, therefore, to present each of the above topics as a separate chapter of the thesis. Each chapter is subdivided into a number of sub-topics and the material for each of these is presented under the following headings;

- (1) Introduction
- (2) Procedure
- (3) Results and discussions

The results pertaining to each of the above three main topics and sub-topics is discussed at the end of each section. Tabulation of some of the data is presented in an Appendix. A chapter on the use of thermodynamics of irreversible processes is added followed by a chapter summarizing the conclusions reached involving the whole investigation.



## Chapter 2.

### CHARACTERIZATION OF THE SOIL SYSTEM

#### 1. Determination of Cation Exchange Capacity of Soil

##### Introduction

Since the cation exchange capacity of a soil is the measure of the quantity of counter-ions required to neutralize the fixed charges of the colloidal complex, it is an important parameter in characterizing the soil system. The soil clay minerals and organic colloidal particles have negative charges that hold dissociable cations. The cation exchange property of soil organic matter is thought to be due to acid ionization of the residual carboxylic (COO-H) groups. Sulfonic and phenolic groups may also be involved. Determining the cation exchange capacity involves measuring the total quantity of negative charges per unit weight of soil. It is not a very exact measurement since its magnitude depends on the nature of the cation employed, the concentration of the salt and the equilibrium pH. However, at a neutral to slightly alkaline pH, 1 N solutions of metallic cations that form strong bases give approximately similar values and these values are by convention accepted as a measure of the cation exchange capacity. One of the most common methods consists of treating the known amount of soil with 1 N ammonium acetate to replace all exchangeable cations; eluting it with either distilled water or 95% ethanol to remove excess  $\text{NH}_4^+$  that is not adsorbed; displacing or replacing the  $\text{NH}_4^+$  adsorbed by some other ion such as  $\text{Na}^+$  in a 10% solution of NaCl, and determining the  $\text{NH}_4^+$  in the replacing solution by quantitative analysis. The use of 1 N  $\text{NH}_4\text{OAc}$  for



extracting the exchangeable cations in soil is advantageous because it is strongly buffered at pH 7, it is effective in wetting the soil and  $\text{NH}_4^+$  is effective in replacing most of the exchangeable cations,  $\text{NH}_4^+$  can be easily volatilized from the displacing solution, and it is suitable for use with flame emission.

Since rubidium has a convenient radioisotope with a half-life of about 19.5 days, it was selected for use in the self-diffusion studies. In the interest of uniformity and in order to be able to correlate the information from other electrochemical measurements, it was decided to use rubidium throughout this study in the form of  $\text{RbCl}$ . Solutions of  $\text{RbCl}$  much more dilute than 1 N were expected to be used for the electrochemical study of soil. Hence, it was suspected that the conventional procedure for measuring C.E.C. using 1 N salt solution as an extractant of the soil might not be satisfactory. Since radioactive measurements were to be made on the soil in the self-diffusion study, it was considered desirable to use radioactive assay for analytical purposes throughout this study.

#### Procedure:

In order to standardize the analytical procedure using a radioisotopic technique, bentonite and kaolinite clays and Dowex 50w-x8 cation exchange resin with known exchange capacities were used, along with the Ponoka loam soil which was to be used for this study. The physical and chemical properties of soil are listed in the appendix, section 1.

Two grams of each of the above exchangers in a 100 ml. centrifuge tube were equilibrated with 50.0 mls. of 1 N  $\text{CaCl}_2$  solution with a





known specific activity of  $\text{Ca}^{45}$ . The equilibrium was confirmed by the specific activity of the solution after equilibration and centrifugation, being identical to that of original solution. An International centrifuge with No. 240 head and 100 mls. tubes was employed. All the clay and soil samples were centrifuged at 2600 r.p.m. for 45 minutes. This gave a centrifugal force of approximately 1900 times gravity and is considered adequate for sedimentation of clays of less than 0.2 microns in diameter. The equilibrium required repeated treatment with successive 50 ml. quantities of solution. Four or five treatments were required for Dowex-50 and even then the ratio of the specific activity of supernatant to that of the original equilibrating solution was only 0.90. In the case of soil and clay two treatments were sufficient to reach the desired ratio of 1.0. The exchangers were then eluted with distilled water and centrifuged until the supernatant solution showed negligible radioactivity. Finally the adsorbed calcium was displaced with 50 mls. of neutral 1 N ammonium acetate solution. The maximum loss due to centrifugation in the original weight of exchanger was about 5% in the case of clay and 10% in the case of soil. In the latter case it was mostly due to undecomposed organic matter that was rejected with the supernatant. One ml. of the extract was dried on a planchet and assayed for  $\text{Ca}^{45}$  with the use of a flow counter. The efficiency for detection of  $\text{Ca}^{45}$  was about 0.4%. Duplicate planchets were always used. They usually showed identical activity. The random errors in the counting at 95% confidence limit were taken into account in determining the activity of the sample. From the known



specific activity of the original equilibrating solutions and the total  $\text{Ca}^{++}$  adsorbed the cation exchange capacity of the exchanger was determined.

### Results and discussion

The known values of exchange capacity given in the appendix section 1 for clays and resins were reproduced within the experimental error of 2-3%. The precision between the four replicates was excellent and gave identical values. In the case of Ponoka Loam a very high value (80 me./100 gm.) for the cation capacity was obtained.

In order to check this value the cation exchange capacity was determined by replacing the exchangeable metallic cations of the soil by 1 N HOAc. The resultant pH change was measured to  $\pm 0.05$  pH units to determine the  $\text{H}^+$  removed from the solution by reference to the standard pH titration curve of acetic acid (Jackson, 1962). To find the cation exchange capacity that is attributable to organic matter a sample of soil was treated with  $\text{H}_2\text{O}_2$  to oxidize the organic matter and the exchange capacity of the resulting sample was also determined by the HOAc method. The exchange capacities for soil with and without organic matter were  $44 \pm 0.6$  and  $17 \pm 0.5$  me. per 100 grams of soil respectively. The value for Ponoka Loam without organic matter was again determined by isotopic exchange with  $\text{Ca}^{45}$  and was found to be  $17 \pm 0.5$  me./100 gm. Thus the high value of exchange capacity by isotopic exchange of  $\text{Ca}^{45}$  was attributable to heavy adsorption of Ca on the organic matter of soil. Since the value of the cation exchange



capacity in the case of organic matter free-soil agreed by both methods (analytical and radioactive tracer), it was considered that the analytical procedure by radioactive assay was satisfactory.

## 2. Determination of Exchange Capacity of Soil by Isotopic Exchange of $\text{Rb}^{86}$

### Introduction

Having thus confirmed the analytical accuracy of the isotopic exchange method, characterization of the soil in terms of  $\text{Rb}^+$  was started. A 0.01 N  $\text{RbCl}$  solution was to be used for diffusion measurements in soil so it was considered desirable to find out the exchangeable  $\text{Rb}^+$  adsorbed on the soil at this low concentration. This was expected to be different from the cation exchange capacity found by conventional methods using 1 N salt solution because of the different level of concentration of the replacing solution. Similarly it was desirable to know if the  $\text{Rb}^+$  was adsorbed solely on the inorganic clay mineral or whether part of it would be adsorbed on the organic matter.

### Procedure:

To oxidize the organic matter, part of the soil sample was treated with  $\text{H}_2\text{O}_2$  as above. Duplicate samples of soil were used in both cases. Identical procedures were used as in the case of isotopic exchange with  $\text{Ca}^{45}$  except that 0.01 N  $\text{RbCl}$  solution tagged with  $\text{Rb}^{86}$  was used. Equilibration to the specific activity ratio of 1 required 3-4 successive treatments. After each addition of 50 mls. of 0.01 N  $\text{RbCl}$  solution, the centrifuge tube with the soil sample was stoppered and shaken on an





electrical end to end shaker for 9 hours before it was centrifuged the supernatant solution was carefully decanted and an additional 50 mls. of solution added. In the isotopic exchange  $\text{Rb}^+$  is much more loosely held and elution with distilled water seemed to release greater quantities of  $\text{Rb}^+$ , originally adsorbed, in successive washings due to hydrolysis. Therefore, no washing was done after the equilibration with 0.01 N  $\text{RbCl}$ . After centrifuging, most of the supernatant solution was carefully removed from the centrifuge tube without disturbing the sedimented soil. As a result of almost 1900 G's of centrifugal force the quantity of  $\text{Rb}^+$  left in free solution in the pores of the cake was considered negligible and was not determined. Since the solution concentration is  $10^{-2}$  N, the error due to addition of  $\text{Rb}^+$  existing in the free solution in relation to that adsorbed was estimated to be less than 1%. The equilibrated soil samples were extracted with 1 N  $\text{NH}_4\text{OAc}$ ; then the filtered extracts were dried on planchets and assayed for  $\text{Rb}^{86}$ . Because  $\text{Rb}^{86}$  emits much stronger radiation than  $\text{Ca}^{45}$  the counting efficiency was 45-50%. Errors at 95% confidence limits were taken into account. From the specific activity of the original solution the me. of  $\text{Rb}^+$  adsorbed was determined.

#### Results and discussion

The results were:

C. E. C. of Ponoka Loam with organic matter       $15 \pm 0.3$  me. /100 gm.

C. E. C. of Ponoka Loam without organic matter       $14 \pm 0.4$  me. /100 gm.

These results show that very little  $\text{Rb}^+$  is adsorbed by the organic matter



in the soil. Since the exchange capacity of the inorganic clay fraction of the soil found by the 1 N HOAc technique was  $17 \pm 0.5$  me./100 gm., this should be the upper limit of  $\text{Rb}^+$  adsorption on the soil.

### 3. Equilibrium Study

#### Introduction

The fact that a 0.01 N solution replaced just as much cation from the clay mineral as a 1 N salt solution was surprising. However, the time required for reaching equilibrium increased and it required almost four times the quantity of 0.01 N  $\text{RbCl}$  compared to the 50 mls. of 1 N  $\text{CaCl}_2$  or HOAc. A study with the objective of determining the  $\text{Rb}^+$  adsorbed on the soil at various dilutions was made. The object was to find the time and quantity of solution at different concentrations of  $\text{RbCl}$  required to establish the equilibrium. The criterion of equilibrium was that the equilibrating solution (after several successive treatments) retained its original specific activity.

#### Procedure

Five concentrations of  $\text{RbCl}$  were used  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , and  $10^{-6}$  molal. They were tagged to a known specific activity and 50.0 mls. were used for a 2.000 gm. sample of soil in a centrifuge tube which was stoppered and shaken for 9 hours before centrifuging. A similar procedure as outlined earlier was followed for centrifuging. After centrifuging the solution was carefully decanted and an additional 50.0 ml. of the same solution was added; the whole process was repeated. All the resulting solutions were saved and their activity was measured. The



ratio of specific activity of the resulting solution to that of the original solution against the time for shaking was determined.

### Results and discussion

Results are plotted in Fig. 3. It can be seen that even after renewing the solution 13-14 times the equilibrium for  $10^{-5}$  m RbCl had not been reached. On the basis of the present results it seems impossible to establish equilibrium at  $10^{-6}$  m RbCl.

#### 4. Mean activity coefficient of RbCl in the soil phase and distribution of $\text{Rb}^+$ and $\text{Cl}^-$

##### Introduction

In modern electrochemical practice the concept of activity of the solute has found widespread use, since it characterizes the non-ideality of the solution. However, in colloidal solution it needs a different perspective since the forces at work and their magnitudes are completely different. The concept of chemical potential is fundamental to a modern treatment of electrolytic solutions. It is defined at constant entropy, volume, charge and composition as

$$\mu_1 = \left( \frac{\delta U}{\delta n_1} \right)_{S, V, n_2, \dots, n_c, e} \quad (2-1)$$

where  $\mu$  is the chemical potential,  $U$  is the energy of the phase,  $n_1$ , the moles of component 1,  $S$ , the entropy,  $V$ , the volume, and  $e$ , the charge. Chemical potential is a thermodynamic quantity with the dimensions of energy per mole. It is a statistical value and does not apply to individual ions. Thermodynamics does not permit the evaluation of the chemical potentials of individual ions. In solutions of electrolytes the requirement







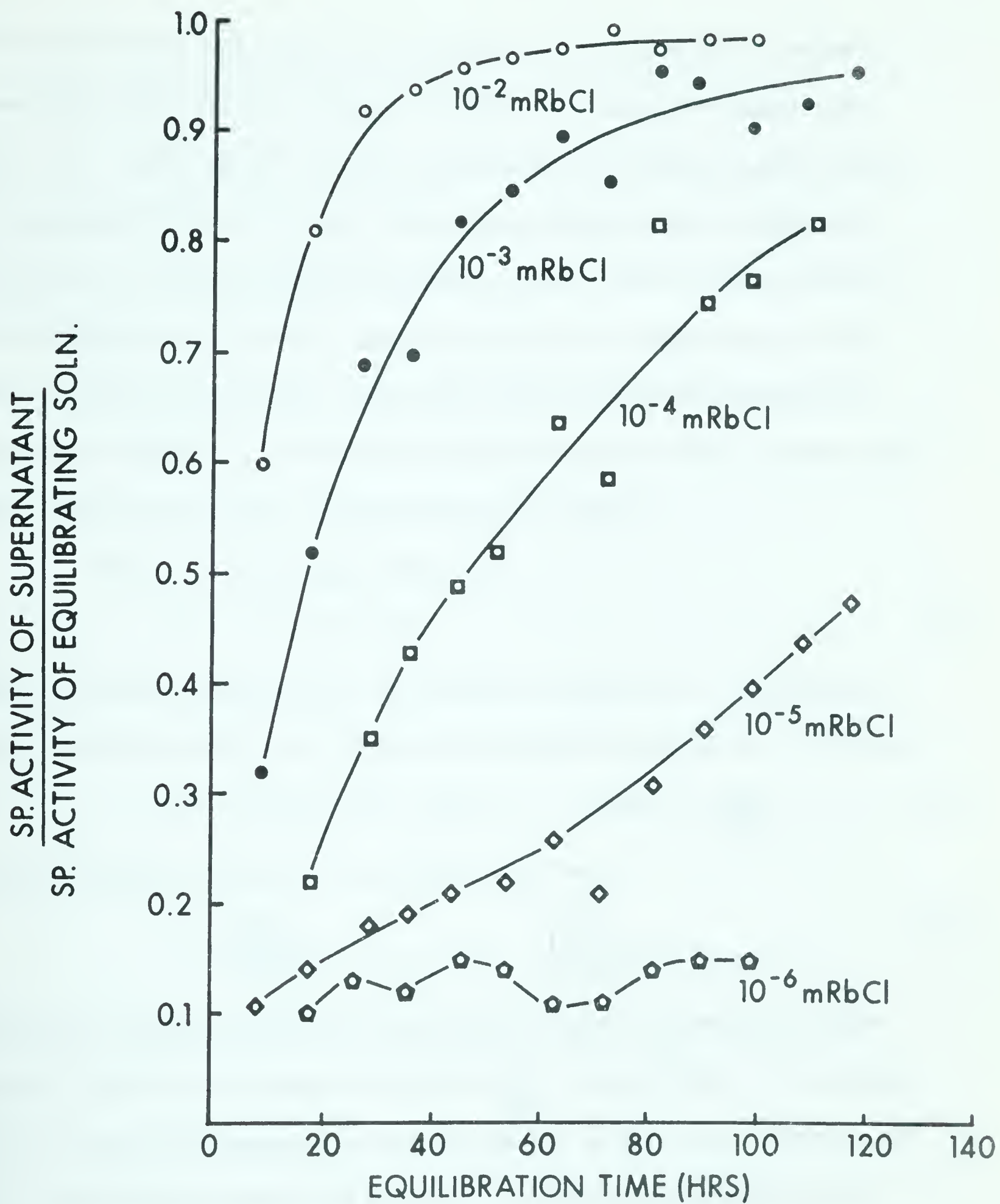


FIG. 3 ESTABLISHMENT OF EQUILIBRIUM BETWEEN THE SOIL PHASE AND THE SOLUTION PHASE



of electro-neutrality imposes the condition that the number of moles of individual ionic species cannot be varied independently as required by Equ. 2-1. Ionic species are the constituents of a solution rather than the components which according to Gibbs is an independently variable constituent of a solution (Harned and Owen, 1956). When it turns out to be permissible to discuss the chemical potential of a single ion e.g.  $\text{Rb}^+$ , for the sake of convenience, this must always mean a thermodynamic function relating to a particular macroscopic system which contains these ions and an electrically equivalent amount of anions.

Gibbs Free Energy is defined by

$$F = U - TS + PV \quad (2-2)$$

where  $P$  is the pressure and  $T$  the absolute temperature. Making allowances for the variation of composition and differentiating Equ. 2-2 we get

$$dF = -SdT + VdP + \mu_1 dn_1 + \dots + \mu_c dn_c + \frac{\delta F}{\delta e} de \quad (2-3)$$

and at constant temperature, pressure and charge

$$\mu_1 = \left( \frac{\delta U}{\delta n_1} \right)_{S, V, n_2, \dots, n_c, e} = \left( \frac{\delta F}{\delta n_1} \right)_{P, T, n_2, \dots, n_c, e} \quad (2-4)$$

where the chemical potential and the partial molal free energy become equal. In the case of solute species the  $\frac{\delta F}{\delta e}$  term of Equ. 2-3 vanishes due to electro-neutrality to retain the equality of Equ. 2-4. However, in the case of ionic constituents this term remains and the partial molal free energy for charged constituents is defined by

$$\left( \frac{\delta F}{\delta n_i} \right)_{P, T,} = \mu_i + z_i F \psi \quad (2-5)$$

Here the assumption that the  $\frac{\delta F}{\delta e}$  term i.e. the free energy gained due



to electric charges would be solely electrostatic in nature and thus can be replaced by  $z_i F \psi$  is implicit.  $\psi$  is the electric potential of the ion due to electrostatic interactions within the phase. Equation 2-5 is simply the definition of the electrochemical potential  $\bar{\mu}$  as defined by Bronstad (1929) and Guggenheim (1929, 1930).

For isothermal conditions Equ. 2-3 and 2-5 can be written as

$$\left( \frac{\delta F}{\delta n_i} \right)_T = V_i dP + \mu_i + z_i F \psi \quad (2-6)$$

Lewis (1901, 1907) defined the activity  $a_i$  of a constituent of a solution by

$$\mu_i = \mu_i^O + RT \ln a_i \quad (2-7)$$

where  $\mu_i^O$  is the chemical potential in some arbitrary standard state,  $a_i$  is the product of the activity coefficient and the concentration and for the present study  $a_i = \gamma_i m_i$  where  $\gamma_i$  is the molal activity coefficient and  $m_i$  is the molality of the solute. Also for the electrolyte dissociating into  $\nu^+$  cations and  $\nu^-$  anions

$$a = a_+^{\nu^+} a_-^{\nu^-} = a_{\pm}^{\nu} \quad (2-8)$$

where  $\nu = \nu^+ + \nu^-$ ,  $a_+$  and  $a_-$  are the conventional individual activities of the ionic constituents and  $a_{\pm}$  is called the mean activity, which can be shown to be

$$a_{\pm} = \gamma_{\pm} m_{\pm} \quad (2-9)$$

where  $\gamma_{\pm}$  is the mean ionic activity coefficient and  $m_{\pm}$  is the mean ion molality.

Thus Equ. 2-6 becomes

$$\bar{F} = \left( \frac{\delta F}{\delta n_i} \right)_T = V_i dP + \mu_i^O + RT \ln m_i + RT \ln \gamma_i + z_i F \psi \quad (2-10)$$





Equation 2-10 completely defines the ionic free molal energy in solution. The activity coefficient  $\gamma_i$  reflects the mutual electrical interaction of the ionic species in the electrolytic solution.

In clay suspensions it is possible that because of the formation of the electrical double layer composed of counter-ions, energy (repulsive) caused by the short range interaction between the ions, and energy of non-coulombic short range interaction between the ion and the particle surface (i. e. nonionic chemical bond), might also contribute to the partial molal free energy of an ionic constituent. At present no estimation of either of these forces is possible. However, the additional terms can all be grouped into the  $RT \ln \gamma$  term of Equ. 2-10. Apart from the recognition of their possible existence not much can be done at present. Thus Equ. 2-10 is completely adequate for colloid solutions if only electrostatic free energy gain is considered.

For uncharged solute species the  $z_i F \psi$  term would disappear and Equ. 2-10 modifies to

$$\bar{F} = V_i dP + \mu_i^0 + RT \ln a_{\pm} \quad (2-11)$$

As pointed out in chapter 1, the present study makes use of a two phase model for the soil-electrolyte system. The soil phase (or what is analogous to the internal phase in most of the work with exchange resins) consists of all the insoluble solid particles, including the charged clay minerals and the electric double layer of the counter-ions (cations) associated with them. The solution phase (external phase in resin terminology) would then be the aqueous solution of an electrolyte at a particular



concentration. At equilibrium between the solution and the soil phase the partial molal free energy of the solute (e. g. RbCl) in the soil phase and in the solution phase should then be equal and one can write Equ. 2-11 as

$$\begin{aligned} \bar{V}_{\text{RbCl}}^{\text{P}} + \mu_{\text{RbCl}}^{\text{O}} + RT \ln \bar{a}_{\pm} \\ = V_{\text{RbCl}}^{\text{P}^{\text{O}}} + \mu_{\text{RbCl}}^{\text{O}} + RT \ln a_{\pm}^{\text{O}} \end{aligned} \quad (2-12)$$

where the barred quantities represent the soil phase and the subscript zero quantities on the right represent the solution phase.

In the present study two assumptions are made: (1) The partial molal volume of the RbCl in soil and solution phase is equal, thus the pressure-volume term on either side of Equ. 2-12 can be neglected even though the pressure in the two phases may not be exactly equal. This has been done before by Bonhoffer (1951), Manecke (1951), Gregor (1953) and Bernstein (1959). (2) The standard state of RbCl in the two phases can be assumed to be identical. "It is important to note that the activity function is much more restricted than either the chemical potential or the partial molal free energy because its definition involves the separate standard state for each phase. Obviously the standard state must be clearly and unambiguously defined before the activity can be given a definite numerical value. Thus the activity of a component of a system at constant temperature and charge is the same in every phase provided that it is defined in each phase in reference to the same standard state." (Harned and Owen, 1958). The standard state of the electrolyte is defined by



$$\lim_{m_{\pm} \rightarrow 0} \frac{a_{\pm}}{m_{\pm}} = 1 \quad \text{or} \quad \lim_{m_{\pm} \rightarrow 0} \gamma_{\pm} = 1 \quad (2-13)$$

The definition of the standard state is based on the assumption that at infinite dilution Henry's law applies to all non-dissociating as well as ionic solute species (Lewis and Randall, 1961). This is true in solution but cannot be verified in the case of colloidal suspensions. If Henry's law is not applicable for adsorbed ionic species  $\bar{\gamma}_{\pm}$  will not approach 1 at infinite dilution. From the results of earlier workers it is seen that as  $m_{\pm} \rightarrow 0$  the  $\bar{a}_{\pm}$  of the adsorbed species also approached zero (Gregor and Gottlieb, 1953; Bernstein, 1959). At infinite dilution there is essentially a one phase system, the internal phase being almost inert, where Equ. 2-13 holds.

With these assumptions Equ. 2-12 can now be written for the equilibrium between the two phases

$$\bar{\gamma}_{\pm}^2 m_{\text{Rb}} \bar{m}_{\text{Cl}} = \gamma_{\pm}^2 m_{\text{Rb}} m_{\text{Cl}} \quad (2-14)$$

and

$$\bar{\gamma}_{\pm} = \gamma_{\pm} \sqrt{\frac{m_{\text{Rb}} m_{\text{Cl}}}{\bar{m}_{\text{Rb}} \bar{m}_{\text{Cl}}}} \quad (2-15)$$

Thus if the molalities are found experimentally and  $\gamma_{\pm}$  in the solution phase is known  $\bar{\gamma}_{\pm}$  in the soil phase can be found.

### Procedure

Experiments to study the change of the mean activity coefficient at different activities of RbCl in the solution phase were designed. Since this information was to be used for the plug potential study reported in chapter 4,





its requirements were kept in mind while designing this experiment. Seven RbCl solutions were so chosen that there were five combinations of them, where within a pair, one of the solutions had twice the activity of the other. The accuracy of the determination of the mean activity coefficients of RbCl in the soil phase depended on the accuracy with which their value was known in the solution phase. Harned (1958) determined the molar activity coefficients of RbCl from diffusion measurements. Since the values of RbCl activity required for the present experiment were different than the ones given by Harned, these were calculated by a trial and error method to the required value. The following Debye-Huckel expression was used for determining the mean rational activity coefficients

$$-\log f_{\pm} = \frac{Az_+z_-\sqrt{I}}{1 + aB\sqrt{I}} \quad (2-16)$$

where  $f_{\pm}$  is the mean rational activity coefficient,  $a$  is  $4 \times 10^{-8}$ , the constants  $A$  and  $B$  are 0.509 and  $0.330 \times 10^8$  respectively and  $I = \frac{1}{2} \sum m_i z_i^2$ . They were converted to the molal or molar activity coefficients by the standard conversion relationship. The values found by the above expression and converted to molar values are compared below with the values given by Harned (1958) and Robinson and Stokes (1959).

Table 1. Comparison of the activity coefficients for RbCl solutions

| Molar conc. | $y_{\pm}$ from Equ. 2-16 | $y_{\pm}$                  |
|-------------|--------------------------|----------------------------|
| 0.005       | 0.9747                   | 0.975 Harned               |
| 0.001       | 0.9649                   | 0.965 "                    |
| 0.015       | 0.9262                   | 0.928 "                    |
| 0.01        | 0.9001                   | 0.901 "                    |
| 0.02        | 0.8672                   | --                         |
| 0.04        | 0.8290                   | --                         |
| 0.06        | 0.7995                   | --                         |
| 0.1         | 0.7623                   | 0.762 Robinson<br>& Stokes |



The above table shows that within the concentration range the Debye-Huckel expression predicts the activity coefficients of RbCl to at least three significant figures and could thus be used to find the activity coefficient for any intermediate concentration. The following solutions were used in the present study.

Table 2. Activities of RbCl solutions used

| Molality   | Mean molal activity<br>coeff. | Mean molal<br>activity |
|------------|-------------------------------|------------------------|
| $m_{\pm}$  | $\gamma_{\pm}$                | $a_{\pm}$              |
| (1) 0.0005 | 0.9747                        | 0.00049                |
| (2) 0.0010 | 0.9649                        | 0.00096                |
| (3) 0.0025 | 0.9462                        | 0.00236                |
| (4) 0.0050 | 0.9262                        | 0.0046                 |
| (5) 0.0102 | 0.8992                        | 0.0092                 |
| (6) 0.0213 | 0.8642                        | 0.0184                 |
| (7) 0.0445 | 0.8198                        | 0.0365                 |

All solutions throughout this study were made from conductivity water distilled from dilute  $\text{KMnO}_4$  and  $\text{NaOH}$ , with specific conductivity  $0.7-1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

The experimental procedure was similar to the previous equilibrium experiment. Triplicate 2.000 gm. soil samples were taken for each solution and equilibrated with solution until a fresh solution lost no ions to the soil (specific activity ratio of 1). The RbCl solutions were tagged with  $\text{Rb}^{86}$  as well as  $\text{Cl}^{36}$ . The moles of  $\text{Rb}^{+}$  and  $\text{Cl}^{+}$  in the soil phase were calculated as described before from the radioactive assay of 1 N  $\text{NH}_4\text{OAc}$  extract of the soil, knowing the specific activity of the original equilibrating solution. Then from Equ. 2-15 the mean activity coefficient of RbCl in the soil phase was calculated. The accuracy of the determination of



the mean activity coefficient also depends on the experimental accuracy of determining the molalities of the  $\text{Rb}^+$  and  $\text{Cl}^-$  ions in the respective phases. This is contingent upon the exact separation of the soil and the solution phase. The technique of centrifuging would leave a thin film of solution around the soil particles in the sedimented soil cake and the ionic concentrations in this film would be counted as belonging to the soil phase rather than to the solution phase. This error was estimated by oven-drying the cake and determining the approximate content of the solution that would be present in the soil cake. As pointed out earlier this error could thus be calculated knowing the concentration of the solution phase and was found to be much less than 0.1% for solutions 1, 2 and 3. It rose to 0.5% for solutions 4 and 5 and was approximately 3 and 6% of the ionic concentration in the soil phase for solutions 6 and 7 respectively.

### Results and discussion

Figure 4 shows the mean activity coefficient of  $\text{RbCl}$  in the soil phase as a function of the concentration of  $\text{RbCl}$  in the solution phase. For the sake of comparison the mean activity coefficients in the solution phase are also plotted on the same graph. Whereas in the solution phase the mean activity coefficient increases on dilution, the reverse is the case in the soil phase. At higher concentrations the mean activity coefficients are expected to be the same in the soil phase and in the solution phase because of the swamping effect as the electrical interactions due to the surface charges of the clay are reduced.

For the free ions of the solution phase (external phase) the ideality of the solution is expected to increase with dilution and hence the







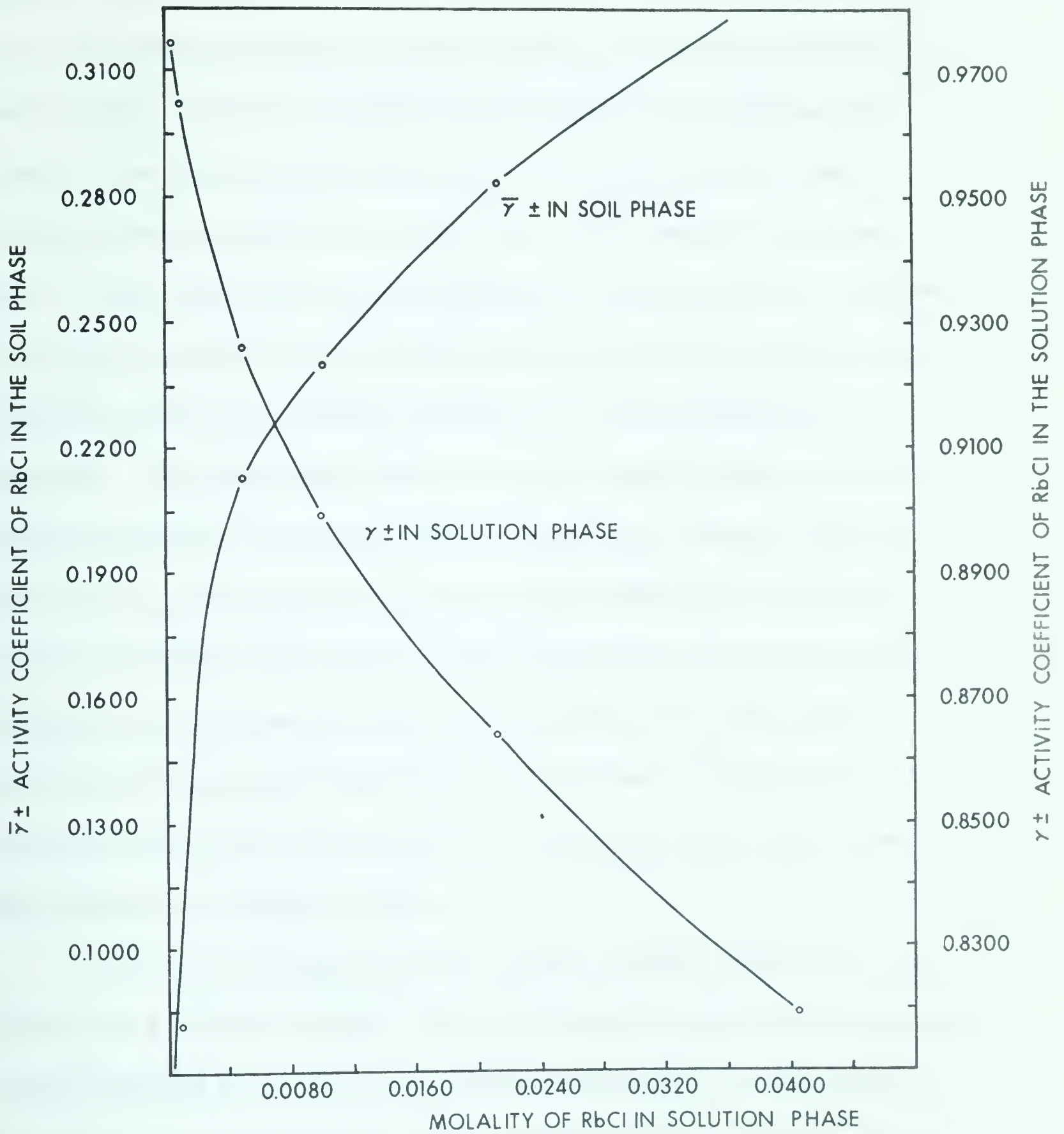


FIG.4 MEAN MOLAL ACTIVITY COEFFICIENT IN THE SOIL PHASE AND SOLUTION PHASE



increase in the activity coefficient, which ultimately reaches 1 at infinite dilution. For the ions adsorbed on the charges of the clay particles the reverse is the case as there is more electrical interaction at decreasing concentration. At lower concentrations the electrical potential in the vicinity of the charge particle increases as postulated by the Gouy-Chapman theory of electrical double layer. This would be expected to cause a reduction in the activity coefficients of the soil phase. However, the sudden increase in the electrical interactions is very striking. As pointed out earlier the pressure-volume terms were assumed to be negligible. This assumption holds for higher concentrations. Below 0.1 molal the pressures in the two phases would be increasingly different, which would be reflected by the mean activity coefficients. However, Gregor and Gottlieb (1953) point out that the pressure-volume term is virtually constant below 0.5 molar concentration. Thus the sharp decrease of  $\bar{\gamma}_{\pm}$  cannot be attributable to the pressure-volume error. A similar trend in the sharp decrease of  $\bar{\gamma}_{\pm}$  in pure clay systems has been reported by Bernstein (1959).

It should be pointed out that the mean activity coefficient in the solution has a definite meaning. Since both cations and anions are present in equal numbers the activity there represents a solute concentration corrected for electrical interactions between the ions. In the case of clay colloids however, the preponderance of cations in comparison to anions near the charged surface would mean that the actual ionic activity coefficients, may be different if they could be determined, from the mean



activity coefficient. The latter is an average of the individual activity coefficients.

In preserving the thermodynamic rigour, perhaps certain simplification of the total effect is unavoidable. However, since  $\bar{\gamma}_{\pm}$  reflects the electrical effect of the charged surface on the ions its value is justified. More will be said about this aspect in the final chapter.

Figure 5 shows the distribution of  $\text{Rb}^+$  in the soil phase as a function of the concentration of the solution phase. The graph resembles the ordinary adsorption isotherm. Scatter in the graph at higher concentrations is probably due to the experimental error involved in excluding the solution phase from the sedimented soil cake. At this concentration the error in estimating the contribution of the salt from the solution phase would be greatly reflected in the soil phase value of  $\text{Rb}^+$ . For working with concentrations higher than used here the present technique is obviously unsuitable. Boyd et al., (1947) developed an equation for ion exchange resin adsorption by formal analogy with the Langmuir equation for adsorption from a binary gaseous mixture. It is as follows

$$\left(\frac{x}{m}\right)_i = \frac{kb_i c_i}{1 + \sum_{j=1} b_j c_j} \quad (2-17)$$

where  $(x/m)_i$  is the amount of  $i^{\text{th}}$  ion adsorbed per unit weight of adsorbant and  $c_i$  is the concentrations in the solution. The terms  $k$  and  $b_i$  are arbitrary constants. For a resin originally saturated with  $\text{B}^+$  and in equilibrium with a solution of  $\text{A}^+$  the above equation takes the form

$$\left(\frac{x}{m}\right)_{\text{A}^+} = \frac{kb_1 c_{\text{A}^+}}{1 + b_1 c_{\text{A}^+} + b_2 c_{\text{B}^+}} \quad (2-18)$$





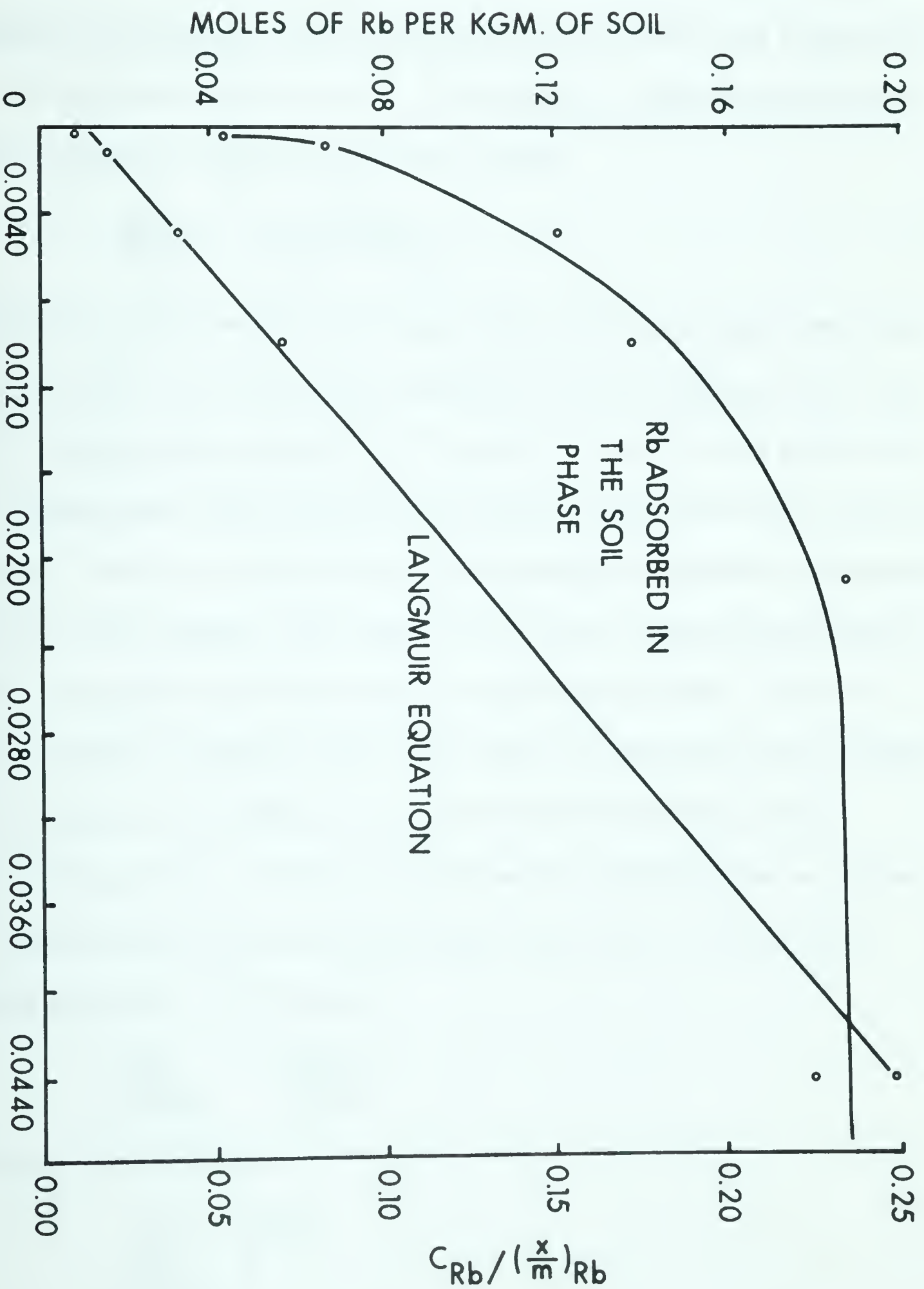


FIG. 5 DISTRIBUTION OF RUBIDIUM IN THE SOIL PHASE AT  
DIFFERENT CONCENTRATIONS OF SOLUTION PHASE



The number of exchanging sites analogous to the the bare surface in the Langmuir treatment, is always small otherwise an appreciable free negative surface charge would be created leading to particles of high negative charge which is not the case. So Boyd et al. neglected the quantity unity in relations to  $(b_1 c_A + b_2 c_B +)$  thus giving

$$\left(\frac{x}{m}\right)_{A^+} = \frac{k b_1 c_{A^+}}{b_1 c_{A^+} + b_2 c_{B^+}} \quad (2-19)$$

It should be pointed out that the Ponoka loam soil in the natural state has more than 60% of its total charge satisfied by the adsorption of  $Ca^{++}$  and  $Mg^{++}$ , the rest being satisfied by  $H^+$ , and  $K^+$ . In the present case as the  $Rb^+$  exchange takes place those ions (originally adsorbed) would come into solution. However, in the process of establishing equilibrium, as pointed out earlier this solution, with some of the cations originally adsorbed on the soil, is replaced by fresh solution containing only  $RbCl$ . This is repeated until no exchange of  $Rb^+$  takes place as indicated by the identical concentration of the solution at equilibrium with that of the original equilibrating solution. Thus at equilibrium the solution phase is a pure  $Rb^+$  system and the term corresponding to  $c_B$  is zero. Thus for the present study Equ. 2-19 becomes

$$\left(\frac{x}{m}\right)_{Rb} = \frac{k b_1 c_{Rb}}{b_1 c_{Rb}} \quad (2-20)$$

which can be modified to

$$\frac{c_{Rb}}{\left(\frac{x}{m}\right)_{Rb}} = \frac{1}{k} c_{Rb} \quad (2-21)$$



Thus if  $c_{\text{Rb}} / \left( \frac{x}{m} \right)_{\text{Rb}}$  is plotted against  $c_{\text{Rb}}$  the graph should be a straight line with the slope of  $1/k$ . Figure 5 shows such a plot of the Langmuir equation from the present experimental data.

Figure 6 shows the corresponding distribution of chloride ions in the soil phase. Since the molality of  $\text{Cl}^-$  in the soil phase is much less in comparison to  $\text{Rb}^+$ , the relative error due to the failure in exact separation of the two phases is much more in the case of  $\text{Cl}^-$  than in  $\text{Rb}^+$ . However, the graph shows clearly that the chloride species are not adsorbed on the soil colloid, a very important observation from the point of view of further development of the problem.





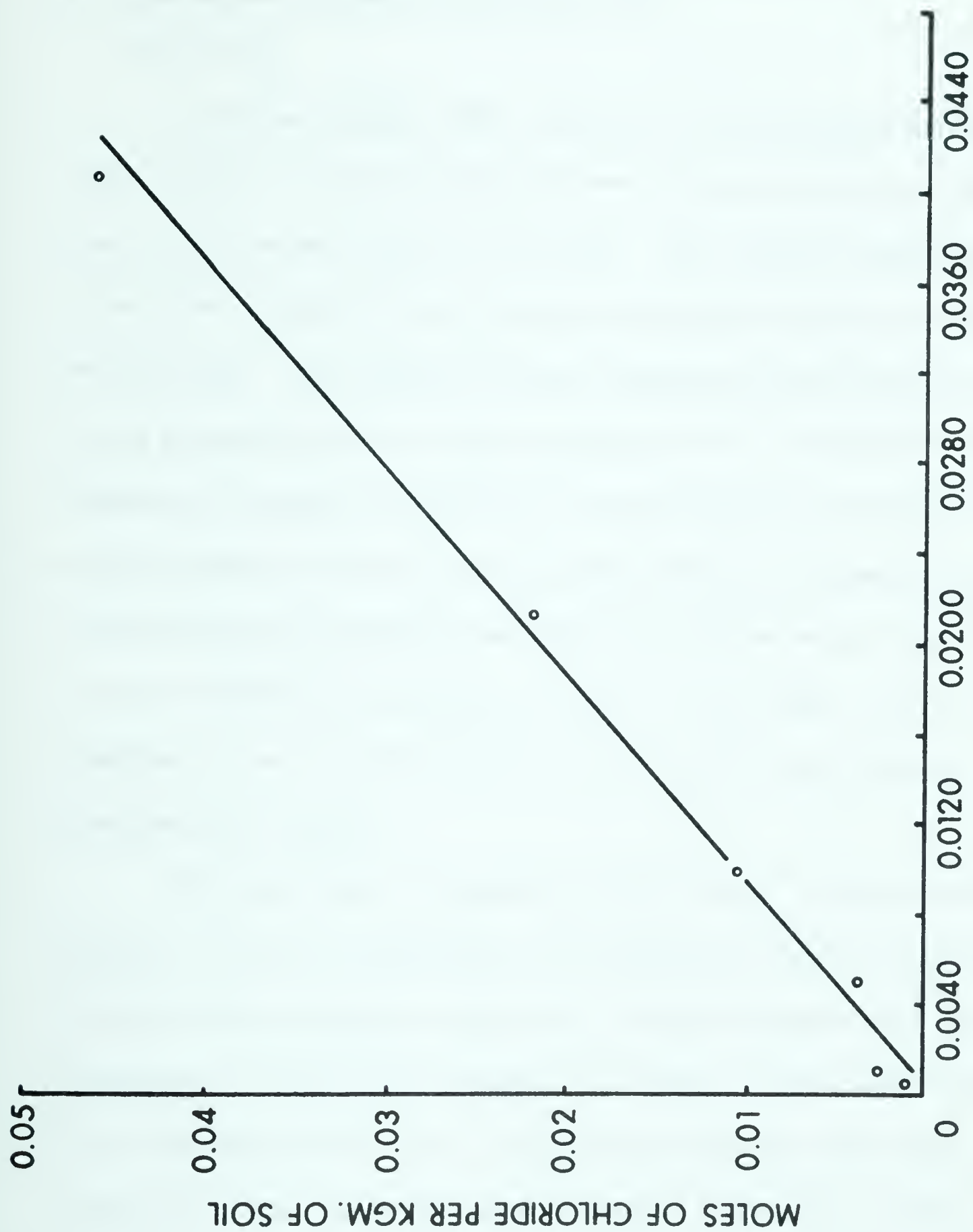


FIG. 6 DISTRIBUTION OF CHLORIDE IN THE SOIL PHASE AT  
DIFFERENT CONCENTRATIONS OF SOLUTION PHASE



### Chapter 3.

#### SELF-DIFFUSION MEASUREMENTS

##### 1. Simultaneous diffusion of $\text{Rb}^{86}$ and $\text{Cl}^{36}$

###### Introduction

In the last chapter (Fig. 5 and 6) it was shown that the distribution of  $\text{Rb}^+$  and  $\text{Cl}^-$  in the soil phase followed different patterns as the concentration of the external solution was varied. The rubidium isotherm was shown to be of the Freundlich type, whereas for the chloride ion a linear isotherm was obtained. The analysis of these isotherms shows that  $\text{Rb}^+$  is adsorbed on the charged sites of the clay particles and  $\text{Cl}^-$  to be practically unadsorbed. Although  $\text{Cl}^-$  might be adsorbed on certain positively charged sites, it is safe to assume from the adsorption data that the consequent free energy change is not much different than that in a solution where chloride ions move from one equilibrium position to another. In this light, one can refer to rubidium as the adsorbed species in the soil phase and chloride as the unadsorbed ionic species.

The mechanism of migration of  $\text{Rb}^+$  and  $\text{Cl}^-$  is thus expected to be different. While the reduction in the diffusion of chloride ions will be solely due to steric hindrance (tortuosity), that for rubidium will be due to adsorption as well as the tortuosity of the path. Thus, following the treatment of Bloksma (1957), one could determine the labyrinth factor 'h', which reflects the effect of the geometrical path in migration, by self-diffusion of chloride and assume (as done by him) that the same factor holds for the diffusion of the adsorbed species as well. Equation 1-13 which was derived from diffusion in clay pastes assumes that the presence of clay particles does not significantly alter the area available for diffusion. This is approxi-



mately the case when clay material up to 10% by weight is used in the paste. But in soil where the actual area is drastically reduced by the presence of the solid matrix, Equ. 1-13 becomes

$$\bar{D}_i = kT w_i \epsilon h \quad (3-1)$$

where  $\epsilon$  is the pore fraction. Since diffusion can take place only through the solution films in the porous medium, the actual area available is the volume fraction of the solution (i. e. volume of solution/total volume). However, when all the pore space is completely occupied by the solution, the so-called saturation stage, the volumetric solution content and pore fractions will be identical.

When this is not so Equ. 3-1 will become

$$\bar{D}_i = kT w_i \bar{\theta} h \quad (3-2)$$

where  $\bar{\theta}$  is the solution content expressed as the fraction of the total volume.

The analogous equation for the adsorbed species is Equ. 1-26

$$\bar{D}_i = kT w_i \bar{\theta} h \frac{d \ln \bar{a}_i}{d \ln c_i} \quad (3-3)$$

If the labyrinth factor 'h' could be found by chloride diffusion, and by knowing  $\bar{D}_{Rb}$ ,  $D_{Rb}^0$  and  $\bar{\theta}$ , one can determine the magnitude of the term  $d \ln \bar{a}_i / d \ln c_i$ . Note that this term corresponds to 'T' of Porter et al., (1960). As shown in the development of the theory this term represents the change in the activity of species i in the soil phase with change in the concentration of the solution phase and is independently determinable.

Since the accuracy of determining  $d \ln \bar{a}_i / d \ln c_i$  hinges on the accuracy with which 'h' is determined, it is worthwhile to consider h in relation to porous media. Analogous to 'h' is the concept of tortuosity used by petroleum geologists. Recently there has been renewed examination of the concept of tortuosity in porous media (Lorenz, 1961). Tortuosity originally





was understood to mean the square of the quotient average length of a flowline divided by the net distance traversed, i.e.  $(L_e/L)^2$ . This concept has its origin in the Kozney-Carman equation (Kozney and Sitzber, 1927; Carman, 1938). Assigning a single value to  $L_e/L$  for a porous medium naturally meets with numerous difficulties for this has some physical meaning only when the requirements of the capillary model are met. This average value for the whole system purports to disregard the presence of individual pores by lumping all the pores together in a single pore. It also assumes that this complex pore has a cross-sectional area per unit bulk area of  $\epsilon$ , normal to the direction of macroscopic flow and an effective length parallel to the macroscopic flow. This would only be true if individual pores are all identical and if the range of pore size is small.

When the porous body can be represented by a bundle of parallel capillaries with a range of radii, a plane section of such a homogeneous body exposes a pore distribution, the total area of which is a fraction of the area of the section. Here then the area available for ion transport is  $\epsilon$ . However, if the capillaries were not so alligned but were randomly oriented and consisted of criss-cross angular bends and configurations, the fraction of the area available is not the pore fraction but  $\epsilon L/Le$  (Porter et al., 1960). The limiting value of this area based upon a model of randomly interconnected capillary tubes of various radii was shown to be  $\epsilon^2$  (Wyllie and Gardner, 1958). Thus depending on where the particular porous system fits the model, the ratio of  $\bar{D}_i/D_0$  would give  $(L/Le)\epsilon$  or  $(L/Le)\epsilon^2$ . Fick's law corresponding to these two cases becomes

$$J_i = -D_i \left( \frac{L}{Le} \right) \frac{dc}{dx} \cdot \epsilon \quad (3-4)$$

$$J_i = -D_i \left( \frac{L}{Le} \right)^2 \frac{dc}{dx} \cdot \epsilon \quad (3-5)$$



When the porous medium conforms to the assumption of a bundle or network of capillary tubes paralld to macroscopic flow, the factor  $(L/L_e)$  as determined by diffusion measurements and by electrical resistivity measurements agrees quite well (Fatt, 1959; Schofield and Dakshinamurti, 1948).

The test of the theory developed in Chapter 1 Equ. 1-26 lies in verifying the term  $d \ln \bar{a}_i / d \ln c_i$  from self-diffusion measurements. This term can be independently determined from the mean activities in the soil phase. This has already been reported in Chapter 2. It should also be pointed out that even though in the development of Equ. 1-26 the area available for diffusion is taken to be  $\epsilon$ , the volume pore fraction, this does not necessarily assume the model of straight capillary tubes. The fact that these capillary channels would have bends and other displacements is taken into account by vectorial treatment of forces and fluxes. However, the assumption of a limited range of angle  $\theta$  is implicit, so that, any tangential displacement of transport is precluded.

In short, depending on whether the area available for ionic transport is  $\epsilon$ , (which would be the case in a model of capillary tubes, with a range of radii, laid parallel to the macroscopic direction) or whether it is  $\epsilon L/L_e$  (Porter et al., 1960) (when the capillary pore has a range of angles  $\theta$  with the direction of macroscopic flow) we get the following relations for nonadsorbed species in a porous medium.

$$\frac{\bar{D}_i}{D_o} = \frac{L}{L_e} \cdot \epsilon \quad (3-6)$$



or

$$\frac{\bar{D}_i}{D_o} = \left( \frac{L}{Le} \right)^2 \epsilon \quad (3-7)$$

Note that the 'h' factor can be either  $(L/Le)$  or  $(L/Le)^2$  depending on the pore geometry. In a porous body of uniform material it is likely that the pore configuration is that of a straight capillary tube laid parallel to the direction of macroscopic flow. In a more complex configuration of pore space Equ. 3-7 would be the rule.

Similarly the electrical resistivity measurements for the above two systems would be

$$\frac{\bar{R}}{R_o} = \left( \frac{Le}{L} \right) \cdot \frac{1}{\epsilon} \quad (3-8)$$

$$= \left( \frac{Le}{L} \right)^2 \cdot \frac{1}{\epsilon} \quad (3-9)$$

where  $R$  is the resistivity of porous media filled with a solution of specific resistivity  $\rho$  and  $R_o$  is the resistivity of the system of identical macroscopic dimensions but devoid of a solid matrix. Schofield and Dakshinamurti (1948) have shown that for porous packings of 'glistening dew', sand, and clay suspensions the right hand side of Equ. 3-6 and 3-8 are equal by diffusion and by electrical resistivity measurements. Fatt (1959) has however obtained a tortuosity factor by resistivity measurement which is the square of that obtained by diffusion measurements. Thus even though the same porous body acts in the case of diffusion like a bundle of capillary channels, parallel to the macroscopic flow, it can change to its complex counterpart during electrical resistivity measurements. This could happen if the lines of force are not







parallel to the length of the pore channels. This brings out the complexities of the geometry of the path followed by an ionic species in diffusion and electrical migration through a porous body.

It has been previously suggested by Bloksma (1959) that the labyrinth factor 'h' in his treatment is not proportional to the pore fraction. On the basis of the above discussion it must be pointed out that this relationship would depend on the model that fits the particular system. To make this point clear, consider Maxwell's Equ. 1-10 for conduction through a continuum of good conductor with spheres of insulator interspersed in the good conductors

$$K = K_s \left[ \frac{1 - \left\{ 1 - \frac{aK_s}{K_p} \right\}^b}{1 + (a - 1)b} \right] \quad (1-10)$$

with  $a = 3K_s / (2K_s + K_p)$  and  $b = V_p / (V_s + V_p)$

where  $K_s$  is the conductivity of the solid, good conductor;  $K_p$  is the conductivity of the pores, the spherical air spaces in the good conductor;  $V_p$  and  $V_s$  are the relative volumes of pore and solid. For the case of diffusion the suffixes must be interchanged i. e. the interspersed spheres are the solid. Thus since the solids have zero diffusivity we get

$$\overline{D}_i = D_o \frac{1}{1 + \frac{(3-1)b}{2}} \quad (3-10)$$

Equation 3-10 is strictly applicable to materials with high porosities and for porous materials such as soil and shales it must be modified by a factor  $f(\epsilon)$ , which takes cognizance of the cross-sectional area available for diffusion. Incorporating this change in Equ. 3-10 we get



$$\overline{D}_i = D_o f(\epsilon) \frac{1}{1 + \frac{(3-1)(1-f(\epsilon))}{2}} \quad (3-11)$$

Now  $f(\epsilon)$  depends on the particular model at work. For capillary tubes of almost uniform radii and lengths parallel to the macroscopic direction  $f(\epsilon) = \epsilon$ ; for the Porter model it is  $f(\epsilon) = \epsilon(L/L_e)$  and for the Wyllie model  $f(\epsilon) = \epsilon^2$ . Perhaps it should be mentioned that Buckingham (1904) who studied gaseous diffusion in soil had used a model similar to that proposed by Wyllie and Gardner (1958) and his  $f(\epsilon) = \epsilon^2$ . Penman (1940) also studied gas diffusion in soil and other porous media; his model corresponds to  $f(\epsilon) = \epsilon$ . For straight parallel tubes Equ. 3-11 becomes

$$\frac{D_i}{D_o} = \frac{2\epsilon}{3-\epsilon} \quad \text{or} \quad \left(\frac{L}{L_e}\right) = \frac{2\epsilon}{3-\epsilon} \quad (3-12)$$

As mentioned in Chapter 1 Penman had arrived at the relation  $\overline{D}_i/D_o = 2/3$  which could be obtained from Equ. 3-12 for small values of  $\epsilon$ .

For Porter's model  $f(\epsilon) = \epsilon(L/L_e)$  and substitution in Equ. 3-11 yields a quadratic in  $(L/L_e)$  with one of the roots resulting in

$$\left(\frac{L}{L_e}\right)^2 = \frac{18-8\epsilon^2}{2\epsilon^2} \quad (3-13)$$

For Wyllie's model with  $f(\epsilon) = \epsilon^2$  we get

$$\left(\frac{L}{L_e}\right)^2 = \frac{2\epsilon^2}{3-\epsilon^2} \quad (3-14)$$

In the present study considerable preliminary work was done on packings of glass beads of sizes 50, 140-210, 230-350, and 500 micron. Simultaneous self-diffusion measurements with  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  were carried out. For packings of beads of uniform size it was found from self-



diffusion measurements that the model applicable was that of  $f(\epsilon) = \epsilon$ . The tortuosity factor ( $L/L_e$ ) was found to increase with decreasing volume of pore fraction. This seems to have the effect of decreasing the radius of the capillary pore where deflections of the ionic species from the macroscopic direction were reduced. Thus packings of granular spheres and solid seem to follow the model of a simple capillary tube with its length paralalled to the macroscopic direction. It is likely that soil will follow such a simple model, however one can never be unequivocal about it. The complex nature of the geometry of the ionic path in the soil was plainly recognized from the beginning of this study. If one is to determine the term  $d \ln \bar{a}_i / d \ln c_i$  from knowledge of 'h', the tortuosity (or labyrinth) factor and compare it to its independently determined value, it was considered imperative to make use of simultaneous self-diffusion of a cation and an anion in order to keep other variables to the minimum. The latter yields the parameter 'h'.

In order to follow the self-diffusion of  $Rb^{86}$  and  $Cl^{36}$  simultaneously it was essential to be able to determine their respective specific activities from the same sample.

#### Procedure

The basis of separation of the total specific activity into the two components (that attributable to  $Rb^{86}$  and  $Cl^{36}$ ) was their different radiation characteristics:

|           | Energy in Mev.       |           | Energy in Mev.    |
|-----------|----------------------|-----------|-------------------|
| $Rb^{86}$ | $\beta^-$ 1.82 (80%) | $Cl^{36}$ | $\beta^-$ 0.714   |
|           | 0.72 (20%)           |           | $Ec(\beta^+)$ 1.2 |
|           | $\gamma$ 1.075       |           |                   |
|           |                      |           |                   |





It is possible to detect  $\text{Rb}^{86}$  activity from the detection of  $\gamma$  rays with the use of a NaI (thallium activated) crystal scintillation counter. However, a  $\beta^-$  counting of  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  by a gas flow counter does not permit the separation of the contributions of  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  from the total  $\beta^-$  count. This was achieved by preparing a standard curve of different  $\text{Rb}^{86}$  samples of known activity and the  $\beta^-$  count obtained from the flow counter. This was subtracted from the total  $\beta^-$  count of the composite sample of  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  to get the  $\beta^-$  count of  $\text{Cl}^{36}$ . Since the accuracy of this measurement depends on the accuracy with which  $\text{Rb}^{86}$  is detected, and its contribution to the  $\beta^-$  count is estimated, all possible care was taken in its detection. The half-life of  $\text{Rb}^{86}$  was determined by conventional method and was found to be 19.77 days (474.7 hrs.). Based on this decay corrections were applied on an hourly basis.

For  $\gamma$ -counting a 'Nuclear Chicago' D55, 2" NaI crystal scintillation probe was used in combination with a C110B automatic sample changer, C111B printing timer and 192B decade scaler. For  $\beta^-$  counting a D47 gas flow detector with helium-butane mixture was used instead of the scintillation probe.

In order to prove the accuracy of the above technique four sets of ten  $\text{Rb}^{86}$  standards of known specific activity were taken and to each of these 0.0025, 0.0050, 0.0075 and 0.01  $\mu\text{C}$  of  $\text{Cl}^{36}$  were added, making a total of 40 samples and these were counted as outlined above.



## Results and discussion

Table 3 below indicates the concentration of  $\text{Cl}^{36}$  found by this technique.

Table 3. Specific activity of  $\text{Cl}^{36}$  detected in known standards ( $\mu\text{c}/\text{ml.}$ )

| $\text{Rb}^{86}$ | $\text{Cl}^{36}$ added |        |        |        |
|------------------|------------------------|--------|--------|--------|
|                  | 0.0025                 | 0.0050 | 0.0075 | 0.01   |
| 0.00024          | 0.0025                 | 0.0049 | 0.0072 | 0.0097 |
| 0.0024           | 0.0026                 | 0.0050 | 0.0073 | 0.0097 |
| 0.0048           | 0.0027                 | 0.0050 | 0.0071 | 0.0096 |
| 0.0071           | 0.0027                 | 0.0049 | 0.0074 | 0.0096 |
| 0.0095           | 0.0027                 | 0.0049 | 0.0072 | 0.0098 |
| 0.0119           | 0.0028                 | 0.0046 | 0.0070 | 0.0089 |
| 0.0143           | 0.0023                 | 0.0053 | 0.0073 | 0.0093 |
| 0.0166           | 0.0026                 | 0.0049 | 0.0067 | 0.0084 |
| 0.0190           | 0.0024                 | 0.0047 | 0.0063 | 0.0090 |
| 0.0214           | 0.0017                 | 0.0049 | 0.0069 | 0.0085 |

The conclusion from this study was that so long as the specific  $\beta$  activity of the composite sample did not exceed 20,000 c.p.m. the radioactive concentration of  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  could, by means of the above technique, be detected with the accuracy of  $\pm 0.0003 \mu\text{c}$  (3-10%).

## 2. Conversion of $\text{HCl}^{36}$ to $\text{RbCl}^{36}$

### Introduction

During some preliminary self-diffusion experiments on packing of glass beads it was found that while  $\frac{\bar{D}_{\text{Rb}} \cdot l}{D_{\text{Rb}}^0 \bar{\epsilon}}$  i.e.  $(L/\text{Le})$  increased with different porosities, the values for  $\frac{\bar{D}_{\text{Cl}} \cdot l}{D_{\text{Cl}}^0 \bar{\epsilon}}$  did not change with porosities. Values of  $\bar{D}_{\text{Cl}}$  were almost the same as  $D_{\text{Cl}}^0$ , with the result that  $(L/\text{Le})$  was different for  $\text{Rb}^+$  and  $\text{Cl}^-$ , which does not agree with theoretical concepts. On examination of the solution that was used for



saturating the packings, it was realized that the low pH of the solution was responsible for this effect. The mobility of hydrogen is very high in comparison to that of  $\text{Cl}^-$  and consequently in keeping the electro-neutrality of the solution, hydrogen could be expected to drag chloride ions along with it. At low pHs this effect is strong enough to mask the effect of tortuosity. Thus the pH of the solution is an important consideration in the case of  $\text{Cl}^{36}$  diffusion.

#### Procedure

$\text{Cl}^{36}$  was obtained in the form of  $\text{HCl}^{36}$ . Conversion of  $\text{HCl}^{36}$  to  $\text{RbCl}^{36}$  was required in order to raise the pH. This was done (Freeman, 1963) by titration of  $\text{HCl}^{36}$  with about 0.1 N  $\text{Rb}_2\text{CO}_3$ . Solutions of  $\text{HCl}^{36}$  were titrated to a pH of 4-5 and then were boiled for a few minutes. They were stoppered and cooled. If the pH was lower than 6.5 the above procedure was repeated until the final solution had a pH of  $6.5 \pm 0.2$ . Since  $\text{Rb}^{86}\text{Cl}$  was also usually dissolved in 0.8 N  $\text{HCl}$ , a similar procedure had to be followed in neutralizing it.

#### Results

When the 0.01 N  $\text{RbCl}$  (with  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$ ) solutions used in glass bead diffusion had a pH between 6 and 6.5 the (L/Le) as obtained from  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  was identical\*.

### 3. Diffusion study

#### Procedure

A diffusion system (Fig. 7) similar to that used by Klute and Letey

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\* For the values of self-diffusion coefficients see Appendix (section 3).







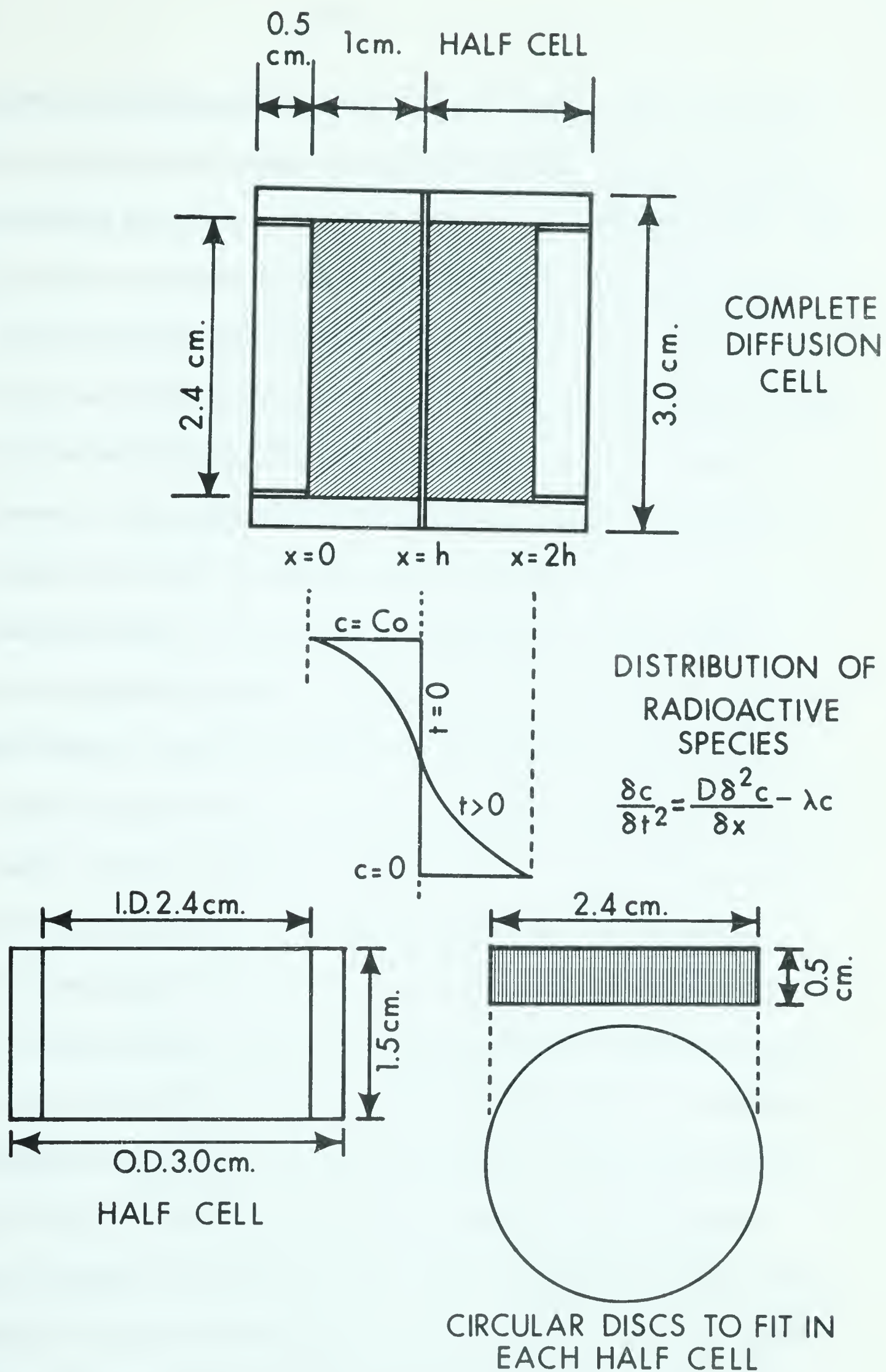


FIG. 7 DIFFUSION CELL



(1958) and Patil (1963) was used. The diffusion system consisted of two half cells containing soil saturated with 0.01 N RbCl. The soil in one of the half cells was saturated with solution tagged with  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$ . The half cells were of equal dimensions, 2.4 cm. in diameter and 1.5 cm. wide. A flat lucite sheet approximately 0.5 cm. thick was cut into circular discs and these were inserted endwise into each half cell to bring the faces of the soil from the radioactive and the nonradioactive half cells in contact. After insertion of the end discs a cylindrical space one cm. high and 2.4 cm. in diameter was left, which contained the weighed amount of soil. The soil sample was Ponoka Loam, whose physical and chemical properties are presented in the appendix (section 1). "Magic Cloth", a porous cellulose cleaning cloth (Sunclo Products, Toronto, Ont.) was placed over the end of each half cell and held with a rubber band. In the container so formed 4.8 gms. of soil was packed uniformly into each half cell. From the experiments on equilibrium (chapter 2) it was known that in order to bring the soil to equilibrium with 0.01 N RbCl solution, three successive portions of solution, approximately in the ratio of 25:1 with soil, were required. This would replace all exchangeable cations with  $\text{Rb}^+$  and would have a solution phase that is 0.01 N in RbCl. Unlike the equilibrium experiment where the soil material was shaken in a centrifuge tube with the solutions of RbCl, here the soil plug in a state of packing had to be equilibrated. Earlier work (Patil, 1963) had shown that this equilibration was very slow and took about ten days, being governed by the diffusion in the soil plugs. In order





to hasten this and to keep the solution circulating through the soil plugs, special platforms, 12" x 10", were constructed from lucite. The top of the platform had perforations. These were placed in a trough with the half cells packed with soil arranged on them. Teflon magnetic stirring bars were placed underneath the platform and these were rotated by electric motors. One set of half cells were thus saturated in a trough containing 0.01 N RbCl tagged with  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$ . The remaining half cells were saturated in an exactly identical fashion in a separate trough with untagged 0.01 N RbCl solution. All the solutions in these experiments were made from water double distilled in a pyrex still with dilute potassium permanganate. The specific conductance was  $0.7 - 1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . Before introducing the solutions into the trough, they were checked for the desired pH, namely  $6.5 \pm 0.2$ . Once the solutions were introduced into the soil, the specific activity measurements were taken frequently. Initially this dropped and subsequently there was a levelling off. At this stage the solutions were carefully siphoned off without disturbing the soil plugs and additional quantities of identical solutions were introduced. The solution to soil ratio was approximately 25:1, the same as used previously in the equilibrium study. The complete equilibrium required two such changes of solution, to achieve a specific activity ratio in radioactive solutions of one. However, due to the long time required for each of these changes (6 - 8 days), the solution was changed only once instead of twice. The specific activity ratio was around 0.90 - 0.92. This introduced an error in the quantity





of  $\text{Rb}^+$  adsorbed on the soil, which was less than 2% at all times. The pH of the solution phase in contact with the soil phase was always found to increase by 0.2 - 0.4 units (6.7 - 6.9). There were three treatments in these experiments:

I. the half cells were drained for half an hour by taking the platform on which the cells were based, out of the solution trough and the half cells, radioactive and nonradioactive counterparts, were brought together in a saturated state;

II. the half cells, radioactive and nonradioactive, were placed on a pressure plate and equilibrated with a pressure of 1/3 atmosphere;

III. the same as II except that a pressure membrane and a pressure of 15 atmospheres was used.

Care was taken to see that there was no contamination of the nonradioactive halfcells by radioactive solutions.

After moisture equilibrium was established the radioactive and nonradioactive half cells were brought together and the cells were sealed in paraffin and stored horizontally in an air bath maintained at  $25 \pm 0.1^\circ \text{C}$ . In the case of treatment I, i. e. in the saturated state, during the process of bringing the halfcells together there is some mixing of radioactive and nonradioactive solutions in the half cells. In order to determine this error the cells were opened immediately after sealing and the extent of mixing determined. This error was always less than 1% in treatment I and almost negligible in treatments II and III.



The basis of the determination of the diffusion coefficient in the present system is to determine the fraction of the total radioactive species transferred to the originally nonradioactive cell as a function of the time elapsed after the start of the diffusion. For each treatment 25 radioactive and 25 nonradioactive half cells were used giving a total of 25 complete cells. The soil plugs in these respective halfcells were brought in contact at a time  $t = 0$  and the diffusion was allowed to proceed for about 500 hours. During the period of diffusion duplicate or triplicate (complete) cells from the original 25 were split open at various times into two halfcells by a razor blade, along the original line of contact of the soil plugs. The soil in these half portions was extracted with 1 N  $\text{NH}_4\text{OAc}$  and the filtered solutions were assayed for  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  by the procedure outlined before. Moisture determination was done for some of the cells by oven drying them at  $110^\circ\text{C}$  for 24 hours. Till  $t = 48$  hrs, the fraction of radioactive species transferred was determined at frequent intervals by separating the cells into the originally radioactive and nonradioactive halves and extracting the soils with 1 N  $\text{NH}_4\text{OAc}$ . After  $t = 48$  hrs, the time intervals of separation of the half cells were spaced till finally all of the remaining cells were separated at  $t = 500$  hrs.

All the solutions that were forced out from the soil plugs during moisture desorption treatments were saved and these were counted along with the other extracts to see if the application of pressure had in any way affected the equilibrium between the soil and the solution phase. If the quantity of radioactive species present in the radioactive halfcell



(i. e.  $x = 0$  to  $x = h$ ) be noted by  $Q_2$  and that within the originally nonradioactive half cell (i. e.  $x = h$  to  $x = 2h$ ) be noted by  $Q_1$ , then for each time of separation an average value of the fraction transferred i. e.  $Q = (Q_2 - Q_1) / (Q_2 + Q_1)$  was determined for each radioactive species ( $Rb^{86}$  and  $Cl^{36}$ ) and these were plotted on a log-log paper against the time of separation after the start of the diffusion.

In order to determine the activation energies of diffusion of  $Rb^{86}$  and  $Cl^{36}$  an exactly identical procedure was used for the treatments I, II, and III except that the cells were maintained at  $20 \pm 0.1^\circ C$  and  $30 \pm 0.1^\circ C$ . This is discussed in more detail in section 4 of this chapter.

Even though  $Rb^{86}$  and  $Cl^{36}$  diffusion was being followed simultaneously, these two processes are completely independent due to some of the precautions taken earlier such as with regard to pH. Such a treatment would reduce the mathematical complexities introduced in the solution of the partial differential equation of diffusion. Thus the following treatment given in terms of a generalized tracer species is applicable to both  $Rb^{86}$  and  $Cl^{36}$ .

The validity of Fick's law of diffusion for soil has been proved (Patil, 1963). The second law, allowing for the decay of the tracer species reads

$$\frac{\partial \bar{c}_i}{\partial t} = \bar{D}_i \frac{\partial^2 \bar{c}_i}{\partial x^2} - \lambda \bar{c}_i \quad (3-15)$$

where  $\bar{c}_i$  is the concentration of the tracer species per unit volume of soil;  $x$  the distance in cm.;  $t$  the time in hrs.;  $\lambda$  the decay constant;  $\bar{D}_i$  the diffusion coefficient in the soil. The boundary conditions for the







diffusion system are

$$(1) \frac{\partial \bar{c}_i}{\partial x} = 0 \quad \begin{matrix} x = 0 \\ x = 2h \end{matrix} \quad @ t > 0$$

(Since this is a closed system there is no net transfer of tracer species

i.e.  $F = \frac{D \partial \bar{c}_i}{\partial x} = 0$ . Since  $D \neq 0$ , therefore  $\frac{\partial \bar{c}_i}{\partial x} = 0$ .)

$$(2) \begin{matrix} \bar{c}_i = \bar{c}_i^0 & 0 < x < h \\ \bar{c}_i = 0 & h < x < 2h \end{matrix} \quad @ t = 0$$

Equation 3-15 can be solved by separation of variables and by Fourier expansion. This solution reads

$$\bar{c}_i = e^{-\lambda t} \left[ \frac{\bar{c}_i^0}{2} + \frac{2\bar{c}_i^0}{\pi} \sum_{m=1}^{\infty} \frac{1}{m} \sin \frac{m\pi}{2} \cos \frac{m\pi x}{2h} e^{-m^2 \pi^2 Dt/4h^2} \right] \quad (3-16)$$

The amount of diffusing substance contained in a layer lying between  $x$  and  $x + dx$  is  $\bar{c}_i A dx$ , where  $A$  is the cross-sectional area of the soil plug. Obtaining  $\bar{c}_i$  from Equ. 3-16 one gets for the amount present between  $0 < x < h$ , i.e.  $Q_2$

$$Q_2 = e^{-\lambda t} \left[ \int_0^h \frac{\bar{c}_i^0}{2} A dx + \int_0^h \frac{2\bar{c}_i^0}{\pi} A \sum_{m=1}^{\infty} \frac{1}{m} \sin \frac{m\pi}{2} \cos \frac{m\pi x}{2h} e^{-m^2 \pi^2 Dt/4h^2} dx \right] \quad (3-17)$$

$$= e^{-\lambda t} \frac{\bar{c}_i^0}{2} Ah \left[ 1 + \frac{8}{\pi^2} \left( e^{-\frac{\pi^2 Dt}{4h^2}} + \frac{1}{9} e^{-\frac{9\pi^2 Dt}{4h^2}} + \dots \right) \right] \quad (3-18)$$

For  $Q_1$ , the amount between  $h < x < 2h$  we get

$$Q_1 = e^{-\lambda t} \left[ \int_h^{2h} \frac{\bar{c}_i^0}{2} A dx + \int_h^{2h} \frac{2\bar{c}_i^0}{\pi} A \sum_{m=1}^{\infty} \frac{1}{m} \sin \frac{m\pi}{2} \cos \frac{m\pi x}{2h} e^{-m^2 \pi^2 Dt/4h^2} dx \right] \quad (3-19)$$

$$= e^{-\lambda t} \frac{\bar{c}_i^0}{2} Ah \left[ 1 - \frac{8}{\pi^2} \left( e^{-\frac{\pi^2 Dt}{4h^2}} + \frac{1}{9} e^{-\frac{9\pi^2 Dt}{4h^2}} + \dots \right) \right] \quad (3-20)$$



Defining  $Q = (Q_2 - Q_1) / (Q_2 + Q_1)$  we obtain

$$Q = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 \pi^2 \frac{Dt}{4h^2}} = \frac{8}{\pi^2} \left[ e^{-\frac{\pi^2 Dt}{4h^2}} + \frac{1}{9} e^{-\frac{9\pi^2 Dt}{4h^2}} + \dots \right] \quad (3-21)$$

The usefulness of Equ. 3-21 will depend upon the rapidity with which the infinite series converges. Obviously large values of  $t$  and  $D$  and small values of  $h$  will favour convergence. In other words, the more nearly the diffusion process has been completed, whether because the tracer species is one that diffuses rapidly or because the time that has elapsed has been long or because the distance to be covered is small or because of any combination of these three factors, the easier it will be to employ Equ. 3-21.

To investigate the convergence of the series in Equ. 3-21  $Q$  was determined at different values of  $Dt/4h^2$  by taking the first two terms of the series. Figure 8 is the plot of these values. As can be seen from the plot for values of  $Dt/4h^2$  less than 0.03 more than one term is required to represent the series. Between values of  $Dt/4h^2 = 0.03$  and 0.05 the error in employing only the first term was less than 1% and for  $Dt/4h^2 > 0.05$  the series was found to converge so rapidly that only the first term was necessary.

### Results and discussion

A plot of  $Q$  against  $t$  was prepared from the experimental values on a log-log scale (Fig. 9). To determine the diffusion coefficient of a tracer species a plot of  $Q$  against  $Dt/4h^2$ , referred to as the theoretical curve was added to Fig. 9. Then these two curves were matched. On a log scale multiplication of two quantities becomes a straight addition and



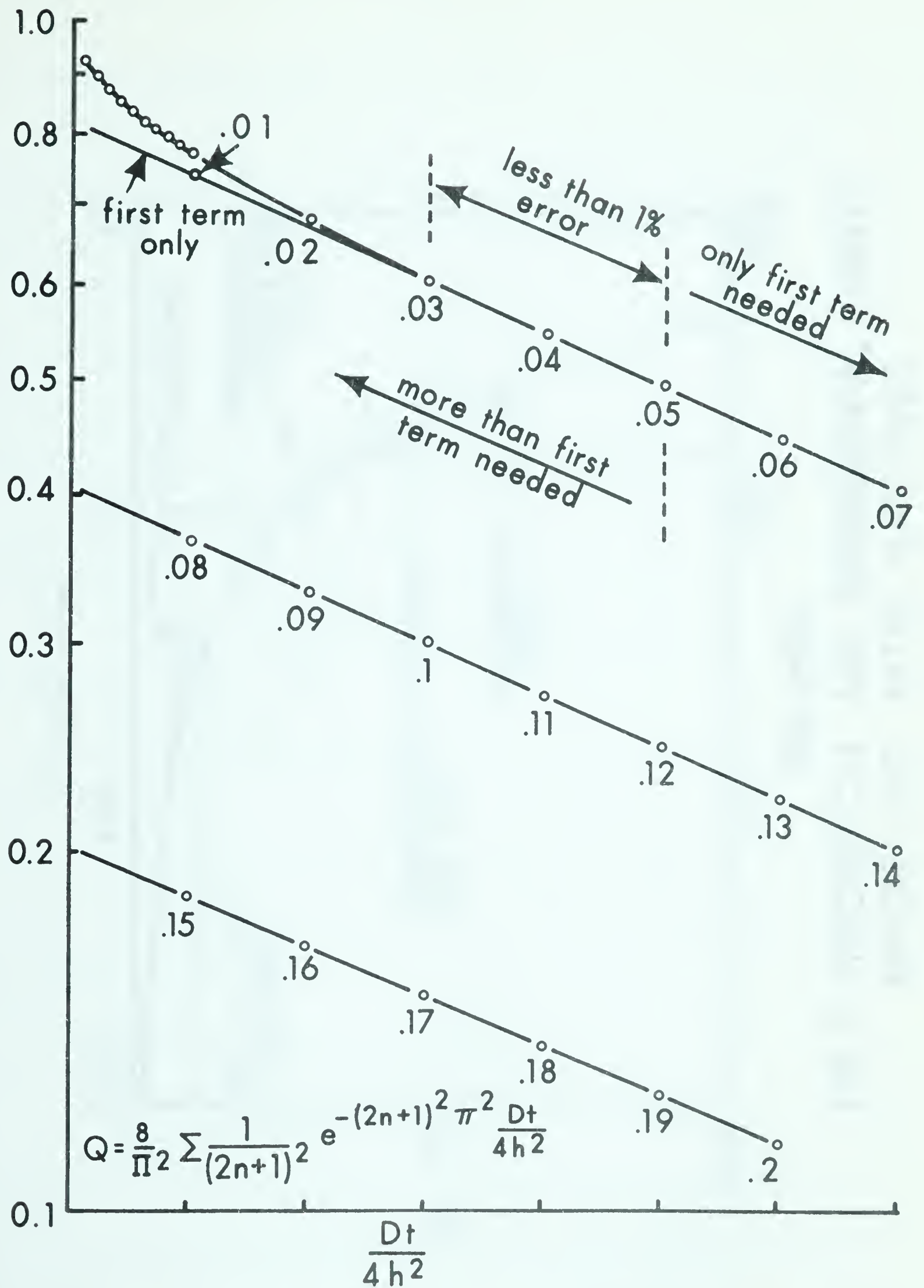


FIG. 8 CONVERGENCE OF SERIES in  $Q$





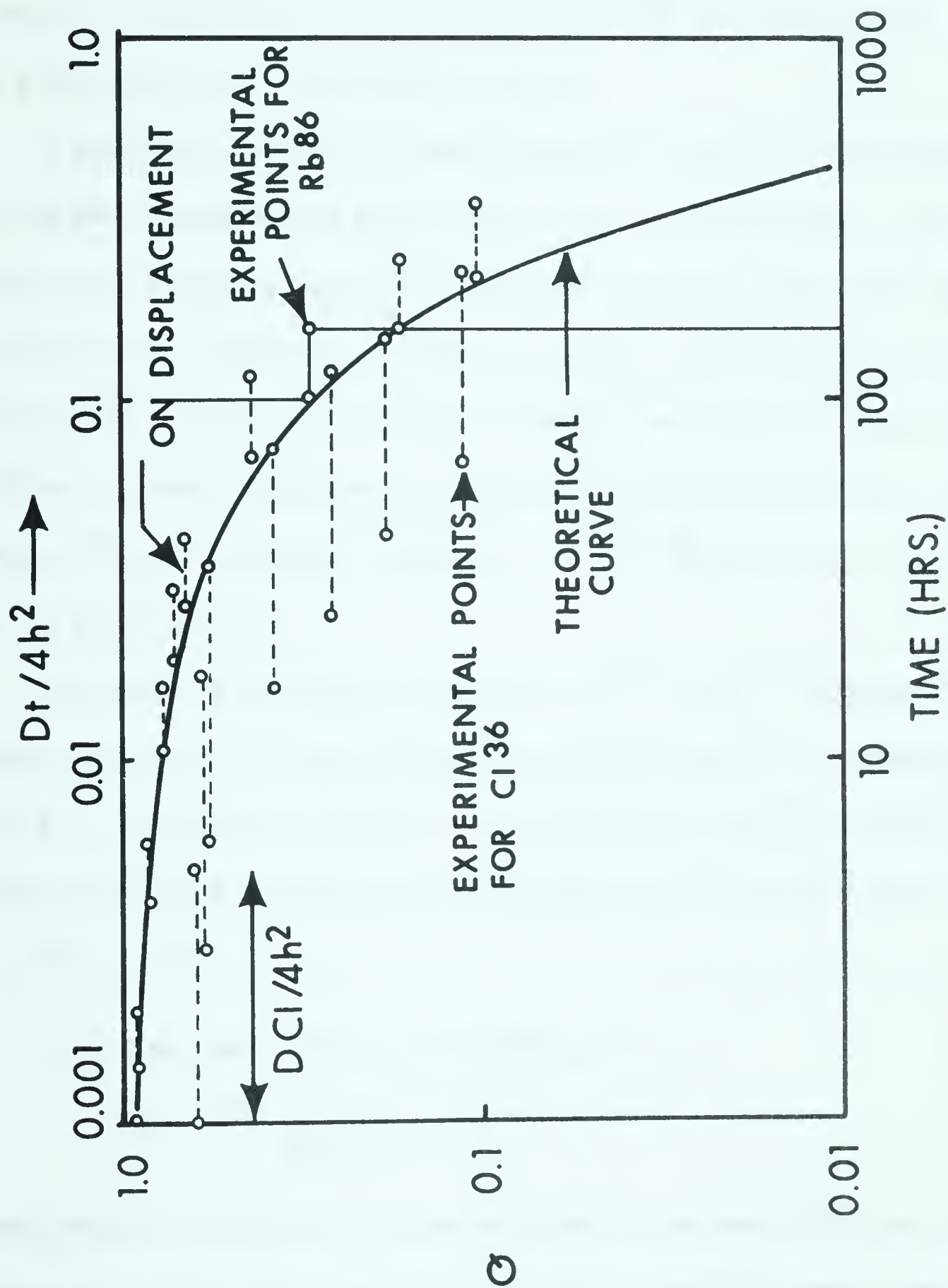


FIG. 9 THEORETICAL AND EXPERIMENTAL CURVES BEFORE AND AFTER MATCHING



since on the x-axis of the plot the only difference for any one value of  $Q$  is  $D/4h^2$  only horizontal displacement of the curve would be expected. Equating this displacement to  $D/4h^2$  the value of  $\bar{D}_i$  was determined, knowing the dimensions of the cell accurately.

As mentioned earlier for small values of  $(Dt/4h^2)$  the representation of the power series by a single term is not accurate enough. However, by taking more points in the region of greater accuracy, this error is more than offset. Moreover, by taking the best fit of the experimental and theoretical curves a true average value for the system is approached. The diffusion measurements were repeated to obtain this precision. While the value of  $\bar{D}_{Rb}$  was exactly reproduced, that for  $\bar{D}_{Cl}$  deviated from the former by less than 3%.

The table of self-diffusion values for  $Rb^{86}$  and  $Cl^{36}$  obtained for the three treatments at various temperatures are listed in the appendix (section 2). The values of self-diffusion coefficients of  $Cl^{36}$  and  $Rb^{86}$  for  $25^\circ C$  were used for determining the labyrinth factor 'h' and the term  $\frac{d \ln \bar{a}_i}{d \ln c_i}$  of Equ. 1-26.

A modified form of Equ. 3-3 for  $\bar{D}_{Rb}$  is

$$\bar{D}_{Rb} = D_o^0 h \frac{d \ln \bar{a}_\pm}{d \ln c_\pm} \quad (3-22)$$

In normal practice the value of  $D_o$  is obtained by the Nernst limiting law by making use of the limiting equivalent conductance of the ionic species.

Thus for  $Rb^+$

$$D_o = \frac{RT}{z_{Rb} F^2} \lambda^0_{Rb} \quad (3-23)$$



$$= 2.661 \times 10^{-7} \frac{\lambda_{\text{Rb}}^{\circ}}{z_{\text{Rb}}} @ 25^{\circ}\text{C} \quad (3-23)$$

where  $\lambda_{\text{Rb}}^{\circ}$  is the limiting equivalent conductance of  $\text{Rb}^{+}$ . The use of Equ. 3-22 for self-diffusion of tracer ion is strictly permissible at infinite dilution or at least in very dilute electrolytic solutions. At appreciable concentrations of solution the self-diffusion coefficient is different from the Nernst limiting value due to the time of relaxation effect. As pointed out earlier, in self-diffusion the solvent displacement is negligible so that the effect of electrophoresis disappears. On the other hand since the cations and anions move relative to one another, the time of relaxation effect is the important factor in self-diffusion.

Onsager (1931, 1945) has discussed the problem of the diffusion of an ion present in vanishingly small amounts in a solution of another electrolyte as a special case of diffusion in multicomponent systems. Gosting and Harned (1951) subsequently showed that his formulae can be applied to the case of self-diffusion. Onsager's equation for self-diffusion coefficient  $D_j^{*}$  of an ion  $j$  present in vanishingly small amounts in an otherwise uniform electrolytic solution becomes

$$D_j^{*} = D_j^{*0} \left[ 1 - \frac{\kappa z_j^2 e^2}{3\epsilon' kT} (1 - d(u_j)) \right] \quad (3-24)$$

where  $D_j^{*0}$  is the self-diffusion coefficient as calculated from the Nernst limiting law,  $\epsilon'$  is the dielectric constant,  $\kappa$  is defined by Equ. 1-1,  $k$  is Boltzman's constant and  $d(u_j)$  is a function of the mobility. The time of relaxation effect in self-diffusion changes the total force by the factor







$$1 - \kappa z_j^2 e^2 \left( 1 - d(u_j) \right) \quad (3-25)$$

The definition of the function  $d(u_j)$  is complicated in the general case covered by Onsager. When the only kinds of ions present are ions 2 and 3 of the main electrolyte and the tracer species 1, the definition of  $d(u_j)$  becomes

$$d(u_1) = \frac{|z_1|}{|z_2| + |z_3|} \left[ \frac{|z_2| \lambda_2^0}{|z_1| \lambda_2^0 + |z_2| \lambda_1^0} + \frac{|z_3| \lambda_3^0}{|z_1| \lambda_3^0 + |z_3| \lambda_1^0} \right] \quad (3-26)$$

Substituting the known constants the final expression at 25°C for a uni-valent electrolyte becomes (Robinson and Stokes, 1959)

$$D_j^* = D_j^{*o} \left[ 1 - 0.7816 (1 - d(u_j)) \sqrt{I} \right] \quad (3-27)$$

where  $I$  is the ionic strength as defined by Equ. 1-3. Based on Equ. 3-26

$d(u_{Rb86}) = 0.4976$  and  $d(u_{Cl36}) = 0.5024$ . By the use of Equ. 3-27 and  $d(u_j)$  values of  $D_{Rb86}^*$  and  $D_{Cl36}^{*o}$  were corrected for the time of relaxation effect at the ionic strength of the soil phase. This correction was very appreciable for  $D_{Rb86}^{*o}$  and  $D_{Cl36}^{*o}$  amounting to almost 12%. Thus in determining the tortuosity factor 'h' (Equ. 3-22) from  $D_{Cl}^o$  the value of  $D_{Cl36}^*$  corrected for the relaxation effect was used instead of  $D_{Cl}^o$ , the Nernst limiting value. Thus Equ. 3-22 becomes

$$\bar{D}_{Cl} = D_{Cl}^* \bar{\theta} h \quad (3-28)$$

$$\bar{D}_{Rb} = D_{Rb}^* \bar{\theta} h \frac{d \ln \bar{a}_i}{d \ln c_i} \quad (3-29)$$

As pointed out in chapter 1, Gast (1962) had obtained the value of ' $\tau$ ' of Porter et al., (1960) (which corresponds to the term  $d \ln \bar{a}_{\pm} / d \ln c_{\pm}$  in the present treatment) which is identical to values of single ion (cation)



activity coefficients as found by Marshall (1951) for identical clay systems by the use of a clay membrane and calomel electrodes. Following the work of Jenny et al. (1950) there had been a controversy about the validity of single ion activity measurements in colloidal suspensions. The ambiguity of such a measurement arose from the assumptions of negligible liquid junction potentials at the salt bridge and the colloidal suspension interface. (Coleman et al., 1950; Marshall, 1950; Peech and McDevitt, 1950; Marshall, 1951; Erikson, 1951; Mysels, 1951; Marshall, 1952; Babcock and Overstreet, 1953; Overbeek, 1953; Bloksma, 1957). The term  $d \ln \bar{a}_i / d \ln c_i$  in Equ. 3-29 has only a quasithermodynamic significance for the single ion activity. The single ion activity coefficients are defined by the following hypothesis of Lewis and Randall (1961):

- i. The activity coefficients of  $K^+$  and  $Cl^-$  are the same in solutions of KCl.
- ii. An ion has the same activity coefficient in all solutions having the same ionic strength. This is an extrapolation of the limiting law behavior of ionic solutions.

With these two assumptions the activity coefficients of simple ionic species may be deduced from the experimental results. Even though the studies of the diffusion potentials in polyelectrolyte solutions have shown that the ambiguities resulting from the liquid junction potentials are likely to be small (Nagasawa et al., 1956), the workers in the field of soil colloidal chemistry have been rather hesitant to accept this, understandably due to difficulties in disproving such an



ambiguity. Because of this the inference that the term ' $\gamma$ ' of Gast and the activity coefficient of the cationic species as found by the clay membrane electrode is the same, is likely to meet with some objections. This did not allow the appropriate inference of the thermodynamic term in Equ. 3-29. It was considered proper to learn about this term with strictly rigorous thermodynamic procedures and to form the conclusions on this basis.

A form of the Nernst-Hartley relation, modified for the present case, to account for the reduction in diffusion due to the tortuosity factor  $h$  can be represented by

$$\bar{D}_{RbCl} = D_{RbCl}^0 \left[ 1 + \frac{(\partial \ln \gamma_{\pm})}{\partial \ln m_{\pm}} h \right] \quad (3-30)$$

where  $D_{RbCl}^0$  is represented by the Nernst-Hartley relation.

$$D_{RbCl}^0 = \frac{|z_+| + |z_-|}{|z_+| \cdot |z_-|} \frac{RT}{F} \frac{u_+^0 \cdot u_-^0}{u_+^0 + u_-^0} \left[ 1 + \frac{\partial \ln \gamma_{\pm}}{\partial \ln m_{\pm}} \right]_{T, P.} \quad (3-31)$$

The last term on the right hand side of Equ. 3-31 is negligible in the case of dilute solutions. The value of  $\bar{D}_{RbCl}$  in Equ. 3-30 was obtained by substituting the mobilities determined by using Equ. 1-31 in the Nernst-Einstein relation which then becomes

$$\bar{D}_{RbCl} = \frac{|z_+| + |z_-|}{|z_+| D_{Rb} + |z_-| D_{Rb}} \bar{D}_{Rb} \bar{D}_{Cl} \quad (3-32)$$

Based on the above Equ. 3-30 for the present soil systems becomes

$$1.035 \times 10^{-6} = 2.05 \times 10^{-5} \left[ 1 + \frac{\partial \ln \bar{\gamma}_{\pm}}{\partial \ln m} \right]_{T, P.} \quad (3-33)$$

from which for the thermodynamic term we get

$$\left[ \frac{1 + \frac{\partial \ln \bar{\gamma}_{\pm}}{\partial \ln m}}{\partial \ln m} \right]_{T, P.} = 0.2382 \quad (3-34)$$





The independently determined value of  $\bar{\gamma}_{\pm}$  for RbCl (chapter 2) is 0.2400.

It should be pointed out that the left hand term in Equ. 3-34 is equivalent to

$$\left[ 1 + \frac{\partial \ln \bar{\gamma}_{\pm}}{\partial \ln m_{\pm}} \right]_{T, P.} = \frac{\partial \ln \bar{a}_{\pm}}{\partial \ln m_{\pm}} \cong \frac{\partial \bar{a}_{\pm}}{\partial m_{\pm}} \quad (3-35)$$

If  $\bar{\gamma}_{\pm}$  behaved as a constant over the range of concentration change involved from solution to soil phase (0.0102 to 0.1387) then

$$\frac{\partial \bar{a}_{\pm}}{\partial m_{\pm}} = \bar{\gamma}_{\pm} \quad (3-36)$$

and then the thermodynamic term in Equ. 3-34 would be equal to

$$\left[ 1 + \frac{\partial \ln \bar{\gamma}_{\pm}}{\partial \ln m_{\pm}} \right]_{T, P.} = \bar{\gamma}_{\pm} \quad (3-37)$$

The fact that the experimental value of  $\bar{\gamma}_{\pm}$  from the self-diffusion measurements coincided with  $\bar{\gamma}_{\pm}$  determined independently on the same system is the confirmation of Gast's results by strictly thermodynamic means. This further elucidates the nature of ' $\gamma$ ' of Porter et al., (1960) and confirms that it corresponds to the activity coefficient of the ionic species itself.

Since the values for a single ion activity coefficient as obtained by diffusion measurements and e.m.f. measurements with clay membrane electrodes (in combination with calomel electrodes) agree (Gast, 1960) it can be said conclusively that the liquid junction potentials in such systems are negligible and that such single ion activity coefficients are physical realities. As pointed out earlier rigorous thermodynamics allows the



use of quantities involving single ionic species as mere fictitious quantities and objects to interpreting them as physical realities. However, if one is seeking tangible explanations in terms of physical forces, rather than the thermodynamic rigour, the single ionic activity coefficients become meaningful (Helfferich, 1962). On this premise Equ. 3-29 for  $\text{Rb}^+$  becomes

$$\bar{D}_{\text{Rb}} = D_{\text{Rb}}^* \bar{\theta} h \bar{\gamma}_{\text{Rb}} \quad (3-38)$$

This equation along with Equ. 3-27 was used to determine  $\bar{\gamma}_{\text{Rb}}$ .

In moisture desorption treatment external pressures are applied on the soil plugs in a specially constructed apparatus. This drains the solution from the plug till the force with which it is held in the plug equals that applied externally. At equilibrium no more solution will be forced out. These desorption techniques are widely used in soil science as well as in petroleum engineering to study the external pressure vs. the saturation of porous media.

The effect of the external pressure is to drain the solution phase and to subject the transport processes to the specific influence of the soil phase. At higher external pressures, e.g. 15 atm., the solution phase could be very severely depleted so that all the transport would take place through the soil phase. As pointed out earlier (chapter 1) the soil phase consists of clay minerals surrounded by the cations (electric double layer).

Table 4 below lists the information obtained for these desorption treatments.



Table 4. Labyrinth factors and single ion activity coefficients for  
Desorption Treatments

| Treatment             | Vol. H <sub>2</sub> O | h     | g     | $\bar{\gamma}_{\text{Rb}}$ |
|-----------------------|-----------------------|-------|-------|----------------------------|
| I. saturated state    | 0.649                 | 0.212 | 0.028 | 0.257                      |
| II. 1/3 atm. pressure | 0.554                 | 0.214 | 0.023 | 0.216                      |
| III. 15 atm. pressure | 0.320                 | 0.088 | 0.014 | 0.577                      |

(The precision in the above treatments, i. e. pressure vs. saturation, was better than 5%.)

In order to investigate the effect of pressure on the ionic equilibrium set up prior to the treatment, all the solutions forced out from the soil plugs were collected and analyzed for ionic content. They were found to be identical to the solution phase indicating little change in the ionic equilibrium. The adsorbed  $\text{Rb}^+$  cations are dissociated from the charged surfaces of the clay particles in the ambient solution, forming an electric double layer. The thickness of this ionic atmosphere is governed by the solution content around the clay micelles. When the solution phase gets depleted the dissociated cations cluster closer to the particles due to contraction of the double layer. This is expected to cause the reduction in the activity coefficient of  $\text{Rb}^+$  due to the increased electrical interaction. This is found to be the case from table 4. The further increase of  $\bar{\gamma}_{\text{Rb}}$  at 15 atm. external pressure can be explained by analogy with the relation between the activity coefficient and concentration of the electrolyte as found in the electrolytic solution. Here with the increase in concentration of solution, the activity coefficients decrease to a minimum, after which they are found to increase





again, sometimes to very high values, exceeding unity. The deviations from the ideal behavior are now in the opposite direction to those which occur at low concentration. It seems plausible that near the clay surface the contraction of the double layer due to severe depletion of the solution phase could bring about such an increase in the activity coefficient of cationic species.

#### 4. Activation Energy of Diffusion in Soil

##### Introduction

The kinetic theory of Absolute Reaction Rates developed by Eyring and his collaborators (Glasstone et al., 1941) has been successful to some extent in describing various related rate processes in terms of the fundamental properties of molecules, their sizes, configurations and interatomic forces (Tuwiner, 1962). It offers a guide to an understanding of the relationship between diffusion, the structure of the medium and the forces at work.

This theory assumes that molecules do not undergo any changes whatever, unless they are first transformed to an intermediate and unstable configuration. Once the molecules attain this transition state they proceed to react at a frequency which is independent of the nature of the reactants and the type of reaction. This frequency (Tuwiner, 1962) is equal to  $\frac{kT}{h}$ ,  $\left[ \frac{1.38047 \times 10^{-6} \text{ erg deg}^{-1}}{6.6242 \times 10^{-27} \text{ erg sec}^{-1}} \right] T$  or  $(2.084 \times 10^{10})T$ , fraction per second which is dependent only upon the absolute temperature,  $T$ . The reciprocal of this quantity or  $4.79894 \times 10^{-11}/T$  seconds represents the time required for the reaction of any activated molecule or complex.



What needs to be determined is the statistical probability that a molecule or configuration of molecules will be activated. This is a function of the Activation energy,  $E$  and the temperature  $T$ . The rate of overall change is determined by the rate at which the transition state is attained and the experimental velocity constant  $k^V$  is given by

$$k^V = k' \frac{kT}{h} \exp (-\Delta F^\# / RT) \quad (3-3)$$

where  $k'$  is a transmission coefficient, normally assumed to be unity in the application of the theory to diffusion and viscosity;  $h$  is Plank's constant; and  $\Delta F^\#$  is the standard free energy of formation.

Water is envisaged as possessing a quasi-crystalline structure which implies the availability of appreciable intermolecular space between loosely packed tetrahedral aggregates of water molecules. The effect of a shearing force is to cause a molecule or a molecular aggregate to move from its original position to a hole in the same liquid layer. During this transfer the migrating molecule passes through the transition state of high energy. In the case of diffusion the driving force is the gradient of chemical potential and energy is required for unlike molecules to slip past one another. If the distance between the two successive equilibrium positions is  $\lambda$ , so that this is the distance through which a molecule of solute is transported in each jump, the change of the standard free energy with distance can be represented by the following diagram.







It should be noted that the theory does not explicitly say whether these equilibrium positions are for solvent or solute. However, for large molecules or ions they are probably those of solvent.

There are two basic assumptions in the present development of the theory (Glasstone et al., 1941).

1. The standard free energy is the same in the equilibrium positions that the molecule occupies in the course of diffusion. Since the concentration at the initial and final positions must be different for diffusion to take place, this condition is applicable only in the case of ideal solution. However, in the case of self-diffusion the above assumption is satisfied as there is no concentration change in the system.
2. If the standard free energy is the same in the initial and the final states and if the energy barrier is assumed to be symmetrical, then the free energy of activation will be the same in the forward and backward directions and thus the specific velocity constant  $k^v$  is the same for the flow in either direction.

In the above diagram  $(c + \lambda dc/dx)$  is less than  $c$  since the concentration decreases in the direction of diffusion,  $dc/dx$  being negative.

The number of molecules moving forward, i. e. from left to right and backward, i. e. from right to left, through the cross section of 1 sq. cm. is given by

$$\begin{aligned} v^f &= Nc k^v \text{ molecules cm. sec}^{-1} \\ v^b &= N(c + \lambda dc/dx) k^v \text{ molecules cm. sec}^{-1} \end{aligned} \tag{3-40}$$





where  $k^V$ , the specific reaction rate is the number of times a molecule moves from one transition state to the next per second. The resultant flow from left to right is

$$v = -N \lambda^2 k^V \frac{dc}{dx} \text{ molecules cm. sec}^{-1} \quad (3-41)$$

Fick's law can also be expressed as

$$v = -DN \frac{dc}{dx} \text{ molecules cm. sec.}^{-1} \quad (3-42)$$

from which we get

$$D = \lambda^2 k^V \quad (3-43)$$

Comparing this with Equ. 3-39 one arrives at the basic equation

$$D = \lambda^2 \frac{kT}{h} \exp. (-\Delta F^\# / RT) \quad (3-44)$$

Making use of the fundamental relation

$$\Delta F^\# = \Delta H^\# - T\Delta S^\# \quad (3-45)$$

where  $\Delta H^\#$  and  $\Delta S^\#$  are the standard enthalpy and entropy of diffusion, we get

$$D = \frac{kT}{h} \lambda^2 \exp(\Delta S^\# / R) \exp. (-\Delta H^\# / RT) \quad (3-46)$$

The experimental energy of activation  $E = RT^2 \frac{d \ln k^V}{dT}$  is related to  $\Delta H^\#$  by

$$E = \Delta H^\# + RT \quad (3-47)$$

From Equ. 3-46 and 3-47 one gets the final result

$$D = \frac{ekT}{h} \lambda^2 \exp. (\Delta S^\# / R) \exp. (-E/RT) \quad (3-48)$$

This has the form of  $D = A \exp (-E/RT)$  and an Arrhenius plot of  $\log D$  against  $1/T$  should be linear, from which  $E$ , the activation energy of diffusion, can be determined assuming that  $kT/h \lambda^2 \exp. (\Delta S^\# / R)$  is independent of temperature.



## Procedure

Self-diffusion measurements were repeated for the three desorption treatments when the cells were stored at  $20 \pm 0.1$  and  $35 \pm 0.1^\circ\text{C}$ . These results along with those already reported for  $25^\circ\text{C}$  were used to determine the activation energies of self-diffusion for  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$ .

## Results and discussion

Figure 10 shows the plots of  $\log D$  vs.  $1/T$  for  $\text{Rb}^{86}$  and  $\text{Cl}^{36}$  for treatments I, II and III. Whereas three points were obtained for  $\text{Rb}^+$  for determining the slope, only two could be obtained for  $\text{Cl}^-$ .

There exists an elaborate theory of diffusion in gases, although a more elementary picture of the diffusion process in gases leads to

$$D = \lambda v / 3 \quad (3-49)$$

where  $\lambda$  is the mean free path of the gas molecules and  $v$  the mean molecular velocity. The diffusion of gas in the adsorbed state is adequately described by an equation of the form

$$D = \frac{1}{4} \frac{a^2}{\tau_0} e^{-E/RT} \quad (3-50)$$

where  $\tau_0$  is the time of oscillation of the molecules or atoms on the adsorbing surface; and 'a' is the distance between adsorption sites. The above equation is derived by Kruyer as reported by deBoer (1953). The time of vibration is proportional to the square root of the molecular weight and volume and also depends upon the distance to neighboring atoms or molecules.  $\tau_0$  refers particularly to vibration perpendicular to the surface of adsorbent.  $\tau_0$  values are between  $10^{-12}$  to  $10^{-14}$  sec. although  $10^{-13}$  has been found to be the most common by Kruyer.



The physical picture underlying the theoretical treatment of diffusion in solids and ionic crystals has also been quite accurately investigated (Jost, 1960). The diffusion in solid is adequately described by

$$D = \lambda^2 \nu \exp (-E/RT) \quad (3-51)$$

where  $\nu$  is the vibration frequency ( $\text{sec}^{-1}$ ) of the particle and  $\lambda$  is the distance between the successive equilibrium positions.  $\nu$  is of the order of magnitude of  $10^{12}$  per second. According to Dushman and Langmuir (1922)  $\nu = E/Nh$ , where  $h$  is the Planck's constant.

The success of treatments of diffusion of gases and solids is mainly the result of understanding the structure of these two states. On the other hand the picture of a liquid state is incomplete. Modern theories of liquid are based upon a model of quasi-crystalline structure of liquid. X-ray investigations have shown the structure of liquids in microscopic regions similar to that of a crystal. Particles in the immediate neighborhood of a central particle in question show a tendency to occupy certain fixed sites, which happen to be those of regular crystal lattice. This tendency, however, decreases rapidly with increasing distance from the central particle. Thus the liquids are said to have only short range order whereas solids have both the short range as well as the long range order. Of course, in contrast to solids, a liquid may contain holes of any size, not only of the size equal to that of the constituent particle. The liquid phase differs from the solid by its greater free volume, by its greater energy (rotational and translational modes) and by its greater entropy, due to the increase in the number of configurations. The Eyring







treatment of diffusion (Equ. 3-48) is found to differ from Equ. 3-50 and 3-51 by the exponential term  $e(\exp\Delta S^\ddagger/R)$  which accounts for the entropy change.

Lai and Mortland (1962) made use of Equ. 3-49 to determine the values of 'a' from self-diffusion measurements in clay pastes assuming  $\tau_0 = 10^{-13}$  sec. They pointed out that even though 'a' values determined in this way are not absolute they have some validity in making comparisons. As pointed out at the beginning of Eyring's theory, his model for the liquid diffusion essentially assumes  $\tau_0 = 1.61 \times 10^{-12}$ , although Dushman and Langmuir (1922) see its dependence on the activation energy E. As can be seen from the above discussion the three treatments are essentially similar except for the introduction of  $\Delta S^\ddagger$  in Eyring's theory of diffusion in liquid. The determination of 'a' from Equ. 3-50 and from 3-51 thus would be tantamount to the assumption of the preservation of short range order and consequent negligible change in the entropy of activation for diffusion.

Table 5 below gives the value of the activation energies obtained for  $\text{Rb}^+$  and  $\text{Cl}^-$  diffusion, the factor  $\lambda (\exp\Delta S^\ddagger/R)^{\frac{1}{2}}$  for each of them and 'a' and ' $\lambda$ ' calculated from Equ. 3-50 and 3-51 respectively. Figure 10 is the Arrhenius plot of the results. The values of a and  $\lambda$  strictly have no significance although they do indicate the effect of entropy change in the diffusion in soil. Normally in diffusion in liquid  $\lambda (\exp\Delta S^\ddagger/R)^{\frac{1}{2}}$  is found to be close to  $2-3 \overset{\circ}{\text{A}}$  which corresponds to the distance between the successive equilibrium positions,  $\Delta S^\ddagger$  being negligible.  $\lambda$  for water has



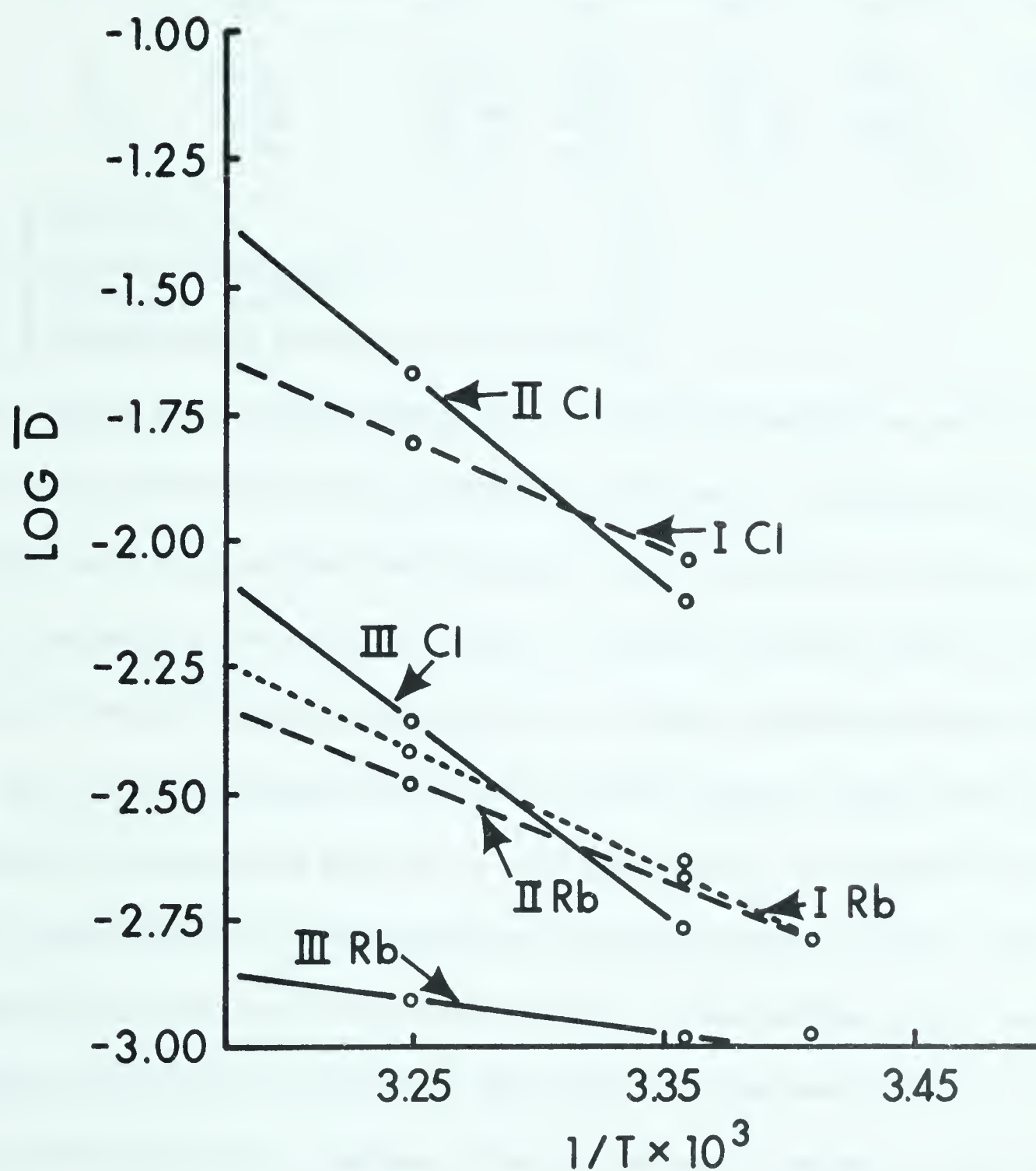


FIG. 10 ARRHENIUS PLOTS FOR SELF DIFFUSION OF RUBIDIUM & CHLORIDE IN THE SOIL



Table 5. Activation Energies for Diffusion in Soil

| Treatment | Acti. Energy<br>(Kcal.) |                 | $\lambda(\exp \frac{\Delta S^\#}{R})$<br>(A°) |                 | 'a'<br>(A°)     | $\lambda$<br>(A°) |
|-----------|-------------------------|-----------------|-----------------------------------------------|-----------------|-----------------|-------------------|
|           | Rb <sup>+</sup>         | Cl <sup>-</sup> | Rb <sup>+</sup>                               | Cl <sup>-</sup> | Rb <sup>+</sup> | Rb <sup>+</sup>   |
| I         | 10.71                   | 10.39           | 381.5                                         | 326.7           | 432.7           | 645.5             |
| II        | 8.61                    | 18.59           | 387.7                                         | 29.54           | 696.5           | 11.59             |
| III       | 3.84                    | 16.47           | 430.2                                         | 36.63           | 6.814           | 0.214             |

$\left[ \begin{array}{l} \text{Values of } \tau_0 - \\ \text{Eyring} - 1.61 \times 10^{-14} \\ \text{Kryuger} - 1 \times 10^{-3} \\ \text{Dushman and Langmuir} 8.9 \times 10^{-15} \end{array} \right]$

been shown to be  $1.5^\circ\text{A}$  (Wang, 1951). Thus the magnitude of this function gives an indication of the mechanism of diffusion. Large positive values of  $\Delta S^\#$  may suggest that the diffusion is accompanied by breakage of bonds or by significant structural changes. Boyd and Soldano (1953) in their study of self-diffusion through cation exchange resins found that  $\Delta S^\#$  for K, Rb, Cs and Ag was close to zero and the values of the above functions closely correspond to that of  $\lambda$ . If higher values of  $\lambda(\exp \Delta S^\# / R)$  indicate the interactions of diffusing species with the charged surface, then this interaction in the soil is massive indeed. To the author's knowledge values for the above function of the order of magnitude found in soil are unknown in any other systems. As pointed out in chapter 1, this difference in the mechanism of diffusion in clay systems and cation exchange resins is to be expected because of the presence of the electric double layer of countercharge in the vicinity of the clay particle. If there is a contraction of this layer due to the exclusion of the solution phase, then the contribution of the cations from this double layer (or from the soil





phase) to the total diffusion would increase and this surface migration would naturally require lower activation energy as is indeed the case. As a result of this contraction attainment of the transition state is expected to be accompanied by considerable positive entropy change as is the case for  $\text{Rb}^+$ .

Contraction of the double layers would produce intense clouds of cations in the vicinity of anions and consequently the activation energy of  $\text{Cl}^-$  is expected to increase. Since removal of trapped chloride ion from such a double layer would produce a more ordered arrangement of cations, the contribution of  $\Delta S^\ddagger$  is expected to be negative as is found in the table.



## Chapter 4.

### ELECTROCHEMICAL MEASUREMENTS

#### 1. A modified D. C. conductance procedure

##### Introduction

The ultimate objective of this work was the measurement of electrolytic conductance in the soil systems. The direct current method of measuring electrolytic conductance has many advantages over the conventional alternating current method. The very simplicity and the absence of the complexities, introduced by capacitance effects in the alternating current method, make the d. c. measurement desirable. The capacitive reactance effects of the electrical double layers on the clay micelle when using alternating current were expected to be appreciable. Low alternating currents of high frequency with the assumptions of negligible reactance effects have been used by Deshpande and Marshall (1959); where the Debye-Falkenhagen effect on the conductance of pure clay systems was reported. Thus it was considered desirable to investigate the use of d. c. conductance methods with the ultimate aim of applying it to soil and clay systems.

One of the main difficulties in the use of the direct current has been the polarization of the electrodes caused by the passage of current through the cell. Many different methods have been tried by various workers to overcome the polarization at the electrodes. Gunning and Gordon (1942) used a direct current method for aqueous alkali halide solutions, their results being comparable to most accurate alternating



current measurements. They used reversible probe electrodes, in addition to the two working electrodes, through which the current was passed. The potential drop across the probe electrodes, during the passage of the current in the cell, gave the measurement of the true resistance of the solution. The presence of potential gradients requires probe electrode of minimum dimension which must be accurately placed for successive measurements. This was achieved by Gunning and Gordon by placing the probe electrode in sidearms of their cell, away from the direct path of the current. The difficulties regarding accurate placement of the probe electrode and the requirement of the reversibility with respect to one of the ionic species in the solution impose limitations on this method. Low (1958) has used a d.c. conductance method for clay suspensions. Ives and Swaroops (1953) overcame the problem of placement and dimensions of the probe electrodes by placing them in the region of the solution where no current passes and hence there was no potential gradient in the vicinity of the probe electrode. However, the extension of probe path reduced the sensitivity of the method (Elias and Schiff, 1956). Elias and Schiff have further extended the d.c. method by using reversible probe electrodes, which are silver-silver halide electrodes mounted in a tube that is surrounded by an alkali halide solution. It is this alkali halide solution that makes contact with the solution in the main cell whose conductivity is to be measured through a liquid junction. Even though the probe electrodes have to be reversible with respect to solution, the formation of a liquid junction enables one to measure the conductance of the solution for which





a reversible electrode is either difficult to prepare or unavailable. This is a decided advantage of this method over all previous ones. The errors introduced due to diffusion of probe solutions or that due to liquid junction potential are negligible and the method has yielded results of high accuracy.

#### Procedure;

The present work is an extension of the method used by Bronsted and Nielsen (1935) where no probe electrodes were used. For measurements in HCl and H<sub>2</sub>SO<sub>4</sub>, they used hydrogen electrodes which served both as working and indicator electrodes. They passed minimum amount of current. Hydrogen electrodes would restrict this method to acids. In the present method ordinary platinized platinum electrodes were used. If the current densities are kept low enough, for most electrolyte solutions, it can be assumed that the passage of small current would bring about electrolysis of water with the production of molecular hydrogen and oxygen at cathode and anode respectively. If the working platinum electrodes behaved as reversible hydrogen and oxygen electrodes it is possible to measure the potential drop across these electrodes soon after a known current is passed through the solution. The hydrogen-platinum electrode is well known as the standard potential datum but the oxygen-platinum had been regarded as irreversible till Bockris (1956) has shown it to be reversible at small current density. The polarization produced at the electrodes by the passage of the current was detected by a vacuum tube voltmeter connected across the platinized platinum electrodes. It was found that this polarization can be eliminated by the passage of current in the reverse direction, indicated by the null reading on the vacuum tube



voltmeter. The current was passed only for a fraction of a second and the potential drop across the platinum electrodes was measured instantaneously after passing the current. By repeating the above procedure of passing the current and eliminating the polarization, it was possible to balance the potentiometer to get the potential drop across the conductivity cell, and the standard resistance.

The cell consisted of a Perspex box 15 x 7 x 5 cm. with a tight fitting cover. The electrodes covered both 5 x 7 cm. ends up to a height of 4 cm. giving an electrode area of 20 cm<sup>2</sup>. The electrodes were sheets of platinum foil glued to the ends of the box with an epoxy resin. The platinum electrode was platinized by the conventional method. The cell was enclosed in polystyrene foam and maintained in an airbath at  $25 \pm 0.1$  °C. The electrical circuit (Fig. 11) consisted of a d.c. power supply for which at first a lead-acid storage cell of about 5/8th charge was used. This is known to give constant potentials. Later a Power Instrument Corp. Model 2230 transistorized stable source was used.  $R_2$  was a Leeds Northrup 100,000 ohm resistance box which served to control the current in the circuit. The double pole double throw switch  $S_1$  allowed the resistance ( $R_1$ ), equal to that at the conductance cell, to be put in the circuit. During measurements resistance ( $R_1$ ) was switched out and the cell switched in so that the current had no load change and hence no surges.  $R_3$  was a calibrated standard resistance of 500 ohms.  $S_2$  and  $S_3$  were coupled double-pole double-throw switches, that changed the polarity of the electrodes as well as aligned the leads of the conductivity cell to that of Leeds Northrup  $K_2$  type potentiometer.





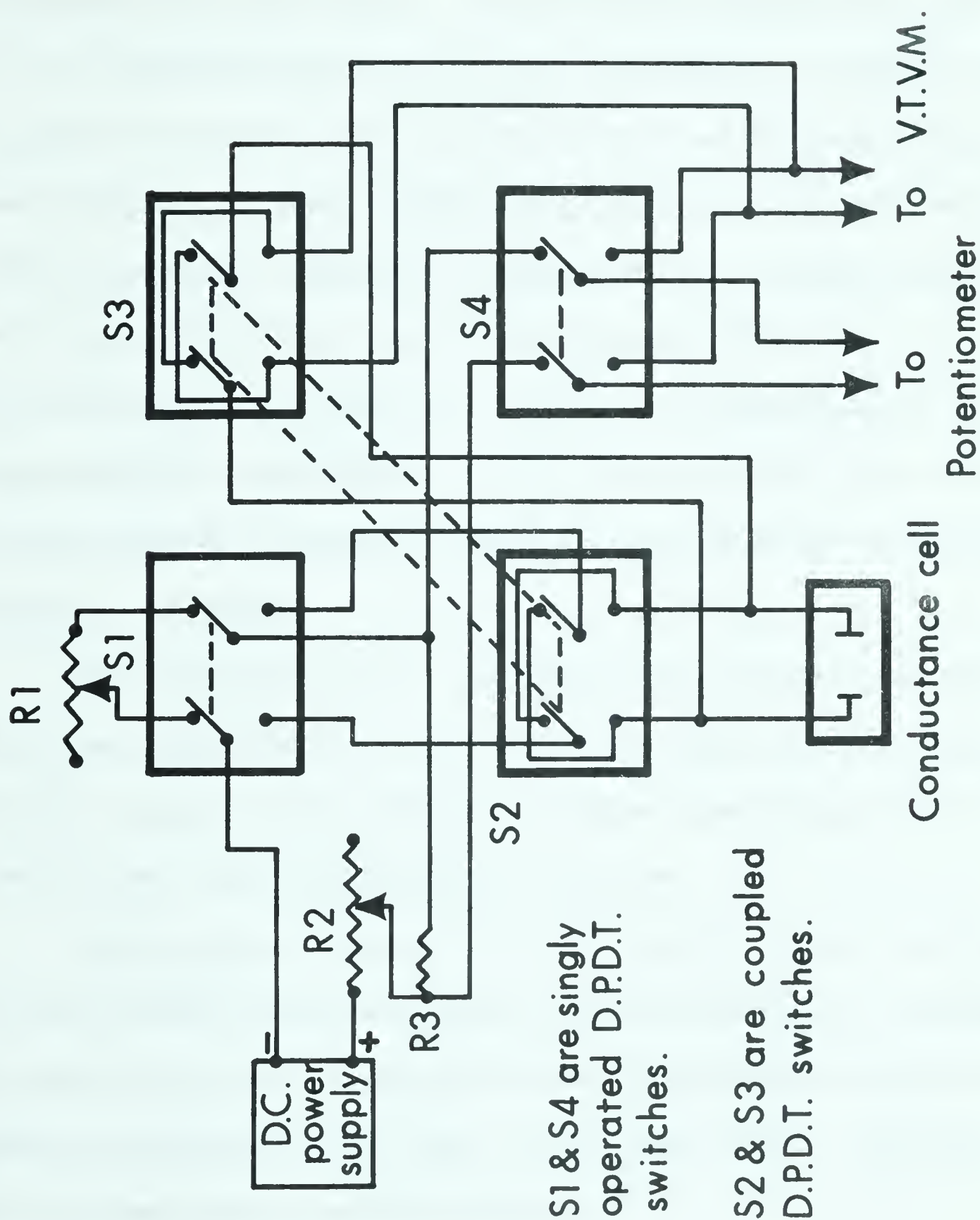


FIG.11 ELECTRICAL CIRCUIT DIAGRAM FOR MODIFIED D.C. CONDUCTANCE PROCEDURE





Load switching was accomplished in the least possible time by the use of Guardian Series 200 relays. The vacuum tube voltmeter used was an R. C. A. Voltomyst with 11 megohms input impedance. In order to check the values of resistance with this method with those obtained by conventional method, a. c. measurements were also made on the same solution. A 1000 c. p. s. A. C. conductance bridge containing a variable capacitor and an Analab Dual Trace Type 1120 Oscilloscope (10  $\mu$ volts/mm. ) as the null detecting device was used. In a series of measurements an a. c. measurement was taken followed by a d. c. measurement. This sequence then was repeated to determine if there was any detectable irreversible change in the solution.

The measurement of d. c. readings initially required as much as 3 hours as depolarizing the system sometimes took as much as 15 minutes. The time required for the reading was reduced considerably with practice, however it was still never less than 1 1/2 hours.

Solutions were prepared with Analar grade KCl twice crystallized and fused at 1000°C and Analar grade Na<sub>2</sub>SO<sub>4</sub> heated to 110°C overnight. The conductivity water was double distilled in a pyrex still from dilute potassium permanganate (Sp. cond.  $1 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>). No vacuum correction was used in weighing the salts.

### Results and discussion

According to Ohm's law, the resistance of the solutions must be independent of the current passed and the best test of the validity of the method was to vary the current and take the potential drop across the



standard resistance ( $E_s$ ) and across the conductivity cell ( $E_c$ ). A constant ratio of  $E_s/E_c$  would evidently provide a test of invariant resistance. Table 6 gives values of this ratio for 0.0052 N KCl with the d. c. method described above.

Table 6. Test for Invariant Resistance

| $E_s$ (Volts) | $E_c$ (Volts) | $E_s/E_c$ | Current density<br>amp/cm <sup>2</sup> |
|---------------|---------------|-----------|----------------------------------------|
| 0.79522       | 1.52875       | 0.5202    | $7.95 \times 10^{-5}$                  |
| 0.70566       | 1.35939       | 0.5151    | $7.05 \times 10^{-5}$                  |
| 0.63492       | 1.22244       | 0.5194    | $6.30 \times 10^{-5}$                  |
| 0.57637       | 1.10937       | 0.5195    | $5.75 \times 10^{-5}$                  |

The values of current density are small and their range is also considerably narrower in comparison to that of Gunning and Gordon (1942), however, the requirement of minimum polarization dictates it. Table 7 compares some of the a. c. and d. c. resistance values for KCl and Na<sub>2</sub>SO<sub>4</sub> solutions at current density of  $4.28 \times 10^{-5}$  amp/cm<sup>2</sup>.

Table 7. Resistance (Ohms) by a. c. and d. c. measurements

| Successive<br>measurements | 0.01 N KCl          | 0.01 N Na <sub>2</sub> SO <sub>4</sub> | 0.1N Na <sub>2</sub> SO <sub>4</sub> |
|----------------------------|---------------------|----------------------------------------|--------------------------------------|
| a. c.                      | 522.0 ( $\pm 0.3$ ) | 631.8 $\pm 0.4$                        | 80.03 $\pm 0.45$                     |
| d. c.                      | 530.3               | 641.7                                  | 90.80                                |
| a. c.                      | 522.8 $\pm 0.2$     | 632.1 $\pm 0.2$                        | 80.00 $\pm 0.32$                     |
| d. c.                      | 529.0               | 641.7                                  | 90.88                                |
| a. c.                      | 522.9 $\pm 0.2$     | 632.1 $\pm 0.5$                        | 80.38 $\pm 0.17$                     |

For both KCl and Na<sub>2</sub>SO<sub>4</sub> solutions, the d. c. values as found by the method were higher than a. c. indicating incomplete depolarization due to activation and ohmic overpotential. However, the d. c. and a. c. difference seems constant for solutions of the same concentration and for similar current density. The literature





values of the specific conductance for 0.01 N KCl, 0.01 N  $\text{Na}_2\text{SO}_4$  and 0.1 N  $\text{Na}_2\text{SO}_4$  are, 0.00141, 0.00112, and 0.00900 respectively whereas those by the present procedure are 0.00139, 0.00115 and 0.00812 respectively (cell constant -0.7378). In the case of KCl solution of concentration higher than 0.01 N, elimination of polarization as indicated above was difficult and the results were erratic.

In general, due to time required for taking individual readings and the necessity of dilute aqueous solution and very low current density, the applicability of the present method as a general d.c. conductance technique may not be very practical and will never compare in accuracy or versatility with the conventional a.c. and Gunning and Schiff's d.c. method. However, there may be special cases, where either the use of reversible probe electrodes is not possible or when the liquid junction technique is undesirable and inconvenient. In such circumstances, the present method may find some use, and for dilute solutions may give results of comparable accuracy.\*

## 2. A conductivity cell for soil and its use

### Introduction

Because of the above reasons it was decided to use the d.c. conductance procedure with silver-silver chloride electrodes for the conductance measurements in soil. A new cell made from Pyrex glass was constructed for the conductance measurements as well as for transport numbers and electroosmotic flow measurements. Figure 12 shows the details of this cell.

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\* For additional data with this method see Appendix (section 5).





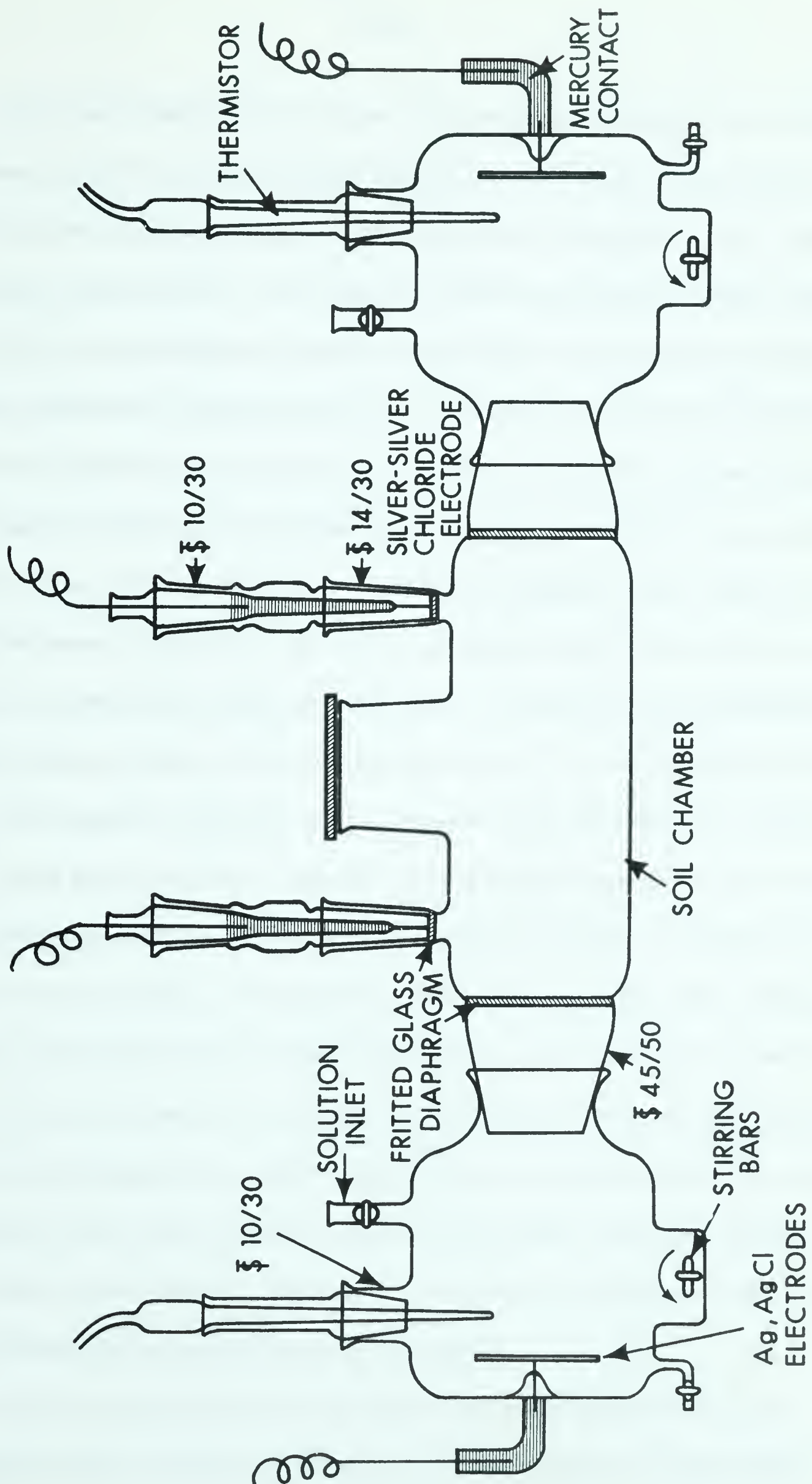


FIG.12 PYREX CELL FOR ELECTROCHEMICAL MEASUREMENTS IN SOIL



The soil chamber 11.37 cms. long was connected to two solution chambers by 45/50 standard taper joints on either side. The volume of this chamber where soil was packed uniformly, through the 4 cm. opening on the top, was 230.6 cc. By means of two standard taper joints, 14/35 and 10/30, arrangement was made to insert Ag/AgCl probe electrodes. In order to prevent soil particles from getting in the vicinity of probe electrode, they were separated from the plug by medium porosity fritted glass discs. Fine porosity fritted glass diaphragms (10-15 $\mu$ ) separated soil from the solution chambers. Solutions chambers were fitted with round platinum electrodes 3.81 cm. in diameter and which were converted to silver-silverchloride electrodes. They were also provided with solution inlets, outlets and chambers for teflon covered magnetic stirring bars. The solution chambers had a capacity of about 1000 ml. of solution each. This large quantity of solution ensured quick equilibrium and produced steady potentials during determination of transport numbers by e.m.f. measurements. Thermistors were inserted into either solution chambers through 10/30 standard taper joints. The thermistors were connected to a recorder for continuous recording of temperature during the period of experiment. The solutions were transferred into the cell by means of jet of CO<sub>2</sub> free air from a pressurized container, which was also used to bubble this air through the solutions, to get rid of the CO<sub>2</sub> dissolved during the preparation of solutions.

In the preparation of Silver-silver chloride electrodes, the potassium silver cyanide was prepared as described by Brown (1934).





An excess of silver cyanide was added to hot filtered solutions containing 20% potassium cyanide. After stirring for about half an hour, the undissolved silver cyanide was filtered off and the solution was cooled. The precipitated potassium silver cyanide was recrystallized. The silver plating solution was made by dissolving 10 gms. of potassium silver cyanide per liter of conductivity water of specific conductance  $1 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ . The free cyanide was reduced to a minimum by adding dilute silver nitrate solution till a faint cloud was produced. After this had settled the clear solution was filtered before use. The current carrying electrodes in the solution chambers were silverplated by filling the conductivity cell itself with potassium silver cyanide solution and by placing the platinum foil anode in the soil chamber. Before silverplating, the electrodes were cleaned in boiling nitric acid. The solution near the electrodes in the chamber was stirred with a magnetic stirrer. For plating both electrodes at the same time, a current density of  $0.37 \text{ ma. / cm.}^2$  was used. After 48 hr. the electrolysis was stopped, the conductivity cell was flushed with conductivity water, and the cathode and the anode chamber were cleaned. In order to remove the excess cyanide dilute silver nitrate solution was added as before to the plating solution. Afterwards the cell was filled with this solution and silverplating was carried on in identical fashion for another 48 hrs. After this the electrodes were washed and stored in strong ammonia solution for 6 hrs., washed again and stored in conductivity water for two days. After this the cell was filled with 0.1 N HCl and the current carrying electrodes were chloridized under stirring, with a platinum cathode in the soil





chamber. The same current density was used as for electroplating of silver and approximately 25% of the silver was converted to silver-chloride. The silverplating was uniform and velvetlike in appearance. The chlorodized electrodes were brownish in color and had a bias potential of less than 0.1 mv. The indicator or (probe) electrodes which consisted of platinum wires about 1/2 cm. long sealed in a glass rod were prepared essentially in the similar manner. A two hour silverplating at the current density of  $2.64 \text{ ma/cm}^2$  was followed by ammonia wash and chloridizing for 30 minutes, at the same current density. The silver/silver chloride electrodes were prepared in batches of four and a pair with least possible bias potentials was selected.

Both electrodes came to equilibrium quickly and developed steady potentials.

## Procedure

### (a) Conductance measurements using solutions

Before the conductance measurements could be carried out on soil material, the cell was calibrated by KCl solutions of different concentration. The bias potentials of probe electrodes were found to increase after use, in spite of careful handling. To overcome this the direction of the current was reversed and the potential drop across the probe electrodes was measured again. Usually the probe electrodes were freshly prepared after one or two runs. Power Instruments Corporation Model 3225 Constant d. c. Power supply was used. Measurements were repeated over a range of current density. During the measure-



ment, continuous recording of temperature was accomplished by means of thermistors hooked to a Yellow Springs Instrument Telethermometer and Y.S.I. Model 80 Laboratory recorder. The maximum temperature fluctuation in the conductivity cell from  $25^{\circ}\text{C}$ . was of the magnitude of  $\pm 0.1^{\circ}\text{C}$ . The conductivity cell was housed in a rectangular copper hood, which was lined continuously with copper tubing. Constant temperature water from a Colora Ultrathermostat NB 31410, was circulated through the copper tubing. The copper hood was insulated from outside by polystyrene foam sheets.

A typical set of measurements are illustrated in Table 8 where  $E_s$  is the potential drop against a 500 Ohm, calibrated standard resistance and  $E_c$  is that against the probe electrodes housed in the soil chamber, which was filled this time with the appropriate solution. Table 9 lists the cell constant obtained by different concentrations of KCl at different times, with the identical procedure outlined in Table 8.



Table 8. D. C. Conductance measurements with 0.01 N KCl

| Es (Volts) | Ec (Volts) | Averages |         | Ec/Es    | Temp.      |
|------------|------------|----------|---------|----------|------------|
|            |            | Es       | Ec      |          |            |
| 1. 0.20301 | 0.13192}   | 0.20299  | 0.13178 | 0.64919} | 25.0 ± 0.1 |
| 0.20298    | 0.13165}   |          |         |          |            |
|            | 0.13179}   |          |         |          |            |
| reverse    |            |          |         |          |            |
| 0.20305    | 0.13267}   | 0.20302  | 0.13260 | 0.65313} | 25.0 ± 0.1 |
| 0.20300    | 0.13253}   |          |         |          |            |
|            |            |          |         | 0.6512   |            |
| 2. 0.36264 | 0.23626}   | 0.36275  | 0.23608 | 0.65081} | 25.1       |
| 0.36277    | 0.23608}   |          |         |          |            |
| 0.36285    | 0.23591}   |          |         |          |            |
| reverse    |            |          |         |          |            |
| 0.36302    | 0.23678    | 0.36302  | 0.23678 | 0.65225  | 25.1       |
|            |            |          |         | 0.6515   |            |
| 3. 0.36243 | 0.23561}   | 0.36243  | 0.23565 | 0.65019} | 25.1       |
| 0.36242    | 0.23568}   |          |         |          |            |
|            |            |          |         |          |            |
| reverse    |            |          |         |          |            |
| 0.36230    | 0.23626}   | 0.36230  | 0.23623 | 0.65202} | 25.1       |
| 0.36230    | 0.23626}   |          |         |          |            |
|            |            |          |         | 0.6511   |            |
| 4. 0.46270 | 0.30131}   | 0.46272  | 0.30118 | 0.65089} | 25.0       |
| 0.46273    | 0.30105}   |          |         |          |            |
|            |            |          |         |          |            |
| reverse    |            |          |         |          |            |
| 0.46277    | 0.30184}   | 0.46276  | 0.30207 | 0.65275} |            |
| 0.46274    | 0.30230}   |          |         |          |            |
|            |            |          |         | 0.6518   |            |
| 5. 0.63847 | 0.41476}   | 0.63818  | 0.41472 | 0.64984} | 0.6508     |
| 0.63807    | 0.41469}   |          |         |          |            |
| 0.63800    |            |          |         |          |            |
| reverse    |            |          |         |          |            |
| 0.63715    | 0.41520}   | 0.63723  | 0.41528 | 0.65169} |            |
| 0.63732    | 0.41536}   |          |         |          |            |

The average  $E_c/E_s = 0.6513 \pm 0.005$

$R_x = 0.6513 \times 500 = 325.7 \pm 0.2$

Cell constant =  $0.00141 \times 325.7 = 0.4592 \pm 0.0003$





Table 9. Summary of Cell Constants

| Solution     | Cell Constant                   |
|--------------|---------------------------------|
| 1. 0.1N KCl  | $0.4598 \pm 0.0013$             |
| 2. 0.01N KCl | $0.4567 \pm 0.0044$             |
| 3. 0.01N KCl | $0.4592 \pm 0.0003$             |
| 4. 0.02N KCl | $0.4587 \pm 0.0014$             |
| 5. 0.02N KCl | $0.4568 \pm 0.0009$             |
| <hr/>        |                                 |
| Average -    | $0.4582 \pm 0.0014 (\pm 0.3\%)$ |

(b) Conductance measurements using soil

For conductance measurements with soil, the central compartment of the conductivity cell was packed with soil. This is done in such a way that the weight of the soil (oven dried at  $110^{\circ}\text{C}$ ) per unit volume was the same as that in the diffusion cell. This volume weight of soil in the conductance cell and in the diffusion cell agreed well at  $0.92 \pm 0.02$  gms./cc. Before packing, 5000 gms. of Ponoka loam soil was thoroughly mixed with 1.5 liters of conductivity water of  $K_{sp} 0.7 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$  and the resulting solution was filtered off with suction by a fine porosity filter candle. This washing was repeated three more times at the end of which the specific conductance of the filtered solution was  $2.32 \times 10^{-4} \text{ Ohm}^{-1} \text{ cm}^{-1}$ . After this 1.5 liter of 0.05 N RbCl solution (highest concentration used in this study) was mixed with the soil cake and the slurry was thoroughly mixed; after 24 hours, during which time the slurry was intermittently stirred, fresh quantities of the same solution was mixed with the soil, after removing the previous solution. This procedure was repeated in all four times and was considered adequate to replace most of the exchangeable cations on the clay micelle with  $\text{Rb}^{+}$ . After the last



RbCl solution was removed the soil was air dried. Since some excess RbCl was left in the pores of the soil cake, due to inability to remove all the solution, the conductivity cell was filled with conductivity water and allowed to stand for 24 hours. It was considered that during this time most of the excess salt would diffuse out of the soil plug. After this the cell (i. e. the solution chambers) were filled with 0. 01N RbCl. The solutions in the chamber were stirred constantly and after 24 hours the solution chambers were emptied and fresh quantities of the same solution were added. After temperature equilibrium the readings were taken. Before starting the experiment, the bias potentials of the electrodes were checked and were found to be 0. 0001 volt. Table 10 lists the results of the d. c. conductance measurements on the soil plug equilibrated with 0. 01N RbCl.

Table 10. D. C. conductance measurement for soil plug with 0. 01N RbCl

|         | Es (Volts) | Ec (Volts) | Averages |         | Ec/Es  | Temp. |
|---------|------------|------------|----------|---------|--------|-------|
|         |            |            | Es       | Ec      |        |       |
| 1.      | 0.15751    | 0.09477    | 0.15753  | 0.09490 | 0.6024 | 25.0  |
|         | 0.15755    | 0.09570    |          |         |        |       |
|         |            | 0.09440    |          |         |        |       |
|         |            | 0.09476    |          |         |        |       |
| reverse |            |            |          |         | 0.5728 |       |
|         | 0.15770    | 0.08587    | 0.15768  | 0.08564 | 0.5431 | 25.0  |
|         | 0.15767    | 0.08536    |          |         |        |       |
|         |            | 0.08571    |          |         |        |       |
| 2.      | 0.19400    | 0.11790    | 0.19396  | 0.11737 | 0.6051 | 25.1  |
|         | 0.19392    | 0.11689    |          |         |        |       |
|         |            | 0.11734    |          |         |        |       |
|         |            |            |          |         |        |       |
| reverse |            |            |          |         | 0.5792 |       |
|         | 0.19403    | 0.10730    | 0.19402  | 0.10734 | 0.5532 | 25.1  |
|         | 0.19400    | 0.10737    |          |         |        |       |
|         |            |            |          |         |        |       |
| 3.      | 0.36017    | 0.21350    | 0.36017  | 0.21350 | 0.5928 | 25.0  |
|         | 0.36017    | 0.21345    |          |         |        |       |
|         |            |            |          |         |        |       |
|         |            |            |          |         |        |       |
| reverse |            |            |          |         | 0.5779 |       |
|         | 0.36049    | 0.20280    | 0.36045  | 0.20291 | 0.5629 | 25.1  |
|         | 0.36040    | 0.20302    |          |         |        |       |
|         |            |            |          |         |        |       |

The average Ec/Es ratio  $0. 5766 \pm 0. 0026$  .  $\therefore R_x = 0. 5766 \times 500 = 288 \pm 1$ . Ohms.



Table 11 gives the corresponding data for the measurements with 0.01N solution (no soil).

Table 11. D.C. conductance with 0.01 N RbCl Solution

|            |            | Averages |         |         | Temp. |
|------------|------------|----------|---------|---------|-------|
| Es (Volts) | Ec (Volts) | Es       | Ec      | Ec/Es   |       |
| 1. 0.15795 | 0.10059}   | 0.15795  | 0.10060 | 0.63691 | 25.1  |
| 0.15794    | 0.10060}   |          |         |         |       |
| reverse    |            |          |         |         |       |
| 0.15800    | 0.09905}   | 0.15799  | 0.09906 | 0.62700 | 25.1  |
| 0.15798    | 0.09907}   |          |         |         |       |
|            |            |          |         | 0.6320  |       |
| 2. 0.25272 | 0.16042}   | 0.25272  | 0.16039 | 0.63465 | 25.0  |
| 0.25273    | 0.16036}   |          |         |         |       |
| reverse    |            |          |         |         |       |
| 0.25282    | 0.15882}   | 0.25282  | 0.15884 | 0.62827 | 25.0  |
| 0.25282    | 0.15885}   |          |         |         |       |
|            |            |          |         | 0.6315  |       |
| 3. 0.36103 | 0.22886}   | 0.36103  | 0.33885 | 0.63388 | 25.0  |
| 0.36103    | 0.22883}   |          |         |         |       |
| reverse    |            |          |         |         |       |
| 0.36113    | 0.22752}   | 0.36112  | 0.22751 | 0.63001 | 25.0  |
| 0.36110    | 0.22750}   |          |         |         |       |
|            |            |          |         | 0.6319  |       |

Average ratio =  $0.6318 \pm 0.0003$

Rx =  $0.6318 \times 500 = 315.90 \pm 0.15$

The specific conductance of the above solution is  $\frac{0.4582}{315.90} =$

$1.450 \pm 0.05 \times 10^{-3} (\pm 0.3\%) \text{ Ohm}^{-1} \text{ cm}^{-1}$ , where  $0.4582 \pm 0.0014$  is the cell constant, i.e. the quotient of 'l' (the distance between the electrodes) and 'a' (the area of the electrodes). The literature value for Ksp of 0.01N RbCl is  $1.446 \times 10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$ . In order to find the specific conductance of the soil plug the cell constant  $lc/\epsilon a$  has to be used since the ions follow a tortuous path in the soil plug. The value of lc is not determinable and so the basic definition of Ksp, the specific conductance, was resorted to. The specific conductance is the current flowing per unit cross-section, per unit potential gradient. So if the current density is known then from the







potential drop one can determine the specific conductance by the relation

$$K_{sp} = \frac{I}{\Delta E / \Delta x} \quad (4-1)$$

where  $I$  is the current density ( $\text{amp}/\text{cm}^2$ ),  $\Delta E$  the potential drop (volts), and  $x$  the distance (cm.).

By the use of Equ. 4-1 the specific conductance of 0.01N RbCl comes to  $1.449 \times 10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$ , which agrees within the experimental error with the value determined by making use of the cell constant. The  $K_{sp}$ , the specific conductance of the soil plug, in a similar fashion works out to be  $1.60 \times 10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$ . The higher conductance of the soil plug compared to the 0.01N RbCl solution could be attributed to the contribution to the conductance by the soil phase (ions in the double layer) and the electro-osmotic flow. Table 10 however shows that over the range of the current density, the contribution of these factors to the total conductance is constant, as shown by nearly constant ratio of  $E_c/E_s$ . However, as the potential drop across the soil plug is further increased it is likely that the soil plug may behave as a non-linear resistance due to contributions from the double layers and electroosmosis which would be a function of applied potential. It may also be pointed out in Table 10 that the difference in the ratio  $E_s/E_c$  at any one current density, depending on the direction of the current can only be due to different geometry of the ionic path, i.e. Le, since differences of this magnitude cannot be explained on the basis of the bias potentials of the probe electrodes.



### 3. Convection conductivity (electroosmosis)

#### Introduction

The contributions by electroosmosis will now be considered. A constant electric field applied to an electrolyte solution causes the cations to migrate to the cathode and the anions to the anode. The electrical potential causes an acceleration of the ions. As the ions accelerate their friction with the surrounding medium increases in proportion to their velocity. The ions finally attain a constant velocity in which the acceleration by the field and the deceleration by the friction balance each other. This steady state is reached almost instantaneously on the application of the potential.

Since an electrolytic solution contains cations and anions in equivalent numbers the electric field imparts equal overall momentum to the cations and anions. As the friction equals the electric driving force, both species convey equal overall momentum to the solvent, and the forces exerted by the cations and anions balance one another exactly irrespective of the difference in rate of migration and ionic valence. A 2-1 valent electrolyte contains twice as many anions as cations, but the electric force acting on the bivalent cations is twice as large as that acting on the monovalent anion, and thus every cation imparts twice as much momentum to the solvent as an anion. As a result of equal momentum imparted to the solvent by cations and anions, no solvent is transferred during the conductance except for the solvation shells.

In cation exchangers, the cations are in the majority and hence



impart more momentum to the solvent than do the anions. The solvent carried along by the counter-ions brings about convection in the direction of the counter-ion transfer. This phenomenon, where the electric current causes not only transference of ions but also convection of the solvent, is called "electroosmosis". The rate of this convection depends chiefly on the counter-ion concentration, the electric field applied and the flow resistance of the ion exchanger (Schmid, 1952). In the ion exchanger, the convection of the pore liquid is superimposed on the migration of the ions relative to the pore liquid. The convective flow of the solvent has a lower linear velocity compared to cations. As the counter-ions 'swim with the fair tide' and the co-ions against the tide, the linear velocity of the counter-ions is higher with respect to co-ions than with respect to the electroosmotic convection of the solvent. Relative to the solid matrix the counter-ions move faster than they would in a stationary liquid. By adding to the rate of counter-ion transfer, the convection of the pore liquid increases the electric conductivity of ion exchange material (Lorenz, 1952; Overbeck, 1953; Schmid, 1952; Spiegler and Coryell, 1953; Staverman, 1952). This surplus conductivity caused by convection is called "convection conductivity".

In the soil plug the pores are considerably larger than the thickness of the electric double layers formed on the clay particles. Thus in the centre of the pore, the liquid content is the electrolytic solution with stoichiometrically equivalent numbers of cations and anions. No electroosmotic flow of solvent is expected here. Since it is only in the diffuse







double layer that there is a preponderance of the cations over anions the contributions of these cations to the conductance is expected to cause electroosmotic flow of solvent. In the soil plugs this contribution from the double layer amounts to about  $10\% \left[ \frac{(1.60 - 1.45 \times 100)}{1.45} \right]$  which compares with the values found by Spiegler (1953) and Despic and Hills (1951). In this light the convection conductivity would be closely related to the 'surface conductance' in Smoluchowski's theory of capillary systems.

The quantitative theory of electroosmosis that is completely satisfactory in all respects has not yet been developed. However, the quantitative treatment of Schmid (1952) as reported by Helfferich (1962) is worth considering and is presented almost verbatim on the next three pages. This treatment is for a particular model of ion exchange porous system which is homogeneous in macroscopic dimensions. No assumptions about the structure of the pores are required. All quantities used (concentrations, fluxes, current density, gradients, etc.) refer to unit volume, cross section, and length of the total ion-exchange material rather than to the pores. The only two quantities used to characterize the pore geometry are the macroscopic flow resistance of the solid matrix to that solvent and the fractional pore volume. It is assumed that the distribution of mobile species within the pores is uniform. This assumption is a good approximation in the usual ion exchange membranes in which the pore width is very small to permit the formation of diffuse double layers. However, this is not so in soil and thus the model is not applicable to the soil in the real sense, even though the treatment to be



developed may apply to the soil system at least in a quantitative way.

A volume element of the ion exchange material, which is in equilibrium before the electric field is applied is considered.

The electric current does not produce any concentration changes and pressure and the transport of mobile species is due solely to electrical transference and the convection. The electric transference,  $(J_i)_{el}$  of the species  $i$  in relation to the surrounding pore liquid, is the product of the rate of motion and the concentration  $\bar{C}_i$  of the species.

$$(J_i)_{el} = -z_i \bar{C}_i \bar{u}_i \text{ grad} \psi \quad (4-2)$$

where  $u_i$  is the velocity under unit force and  $\text{grad} \psi$  is the gradient of the electrical potential. In the ion exchanger the transference relative to the matrix results from the superposition of the transference relative to the pore liquid and transport by convection of the pore liquid. According to thermodynamics of irreversible processes (de Groot, 1951) the contribution from the convection is the product of the concentration  $\bar{C}_i$  and the rate  $v$  at which the centre of gravity of the pore liquid moves.

$$(J_i)_{ion} = \bar{C}_i v \quad (4-3)$$

Thus the transference of the ion  $i$  is equal to

$$J_i = (J_i)_{el} + (J_i)_{ion} = z_i \bar{C}_i \bar{u}_i \text{ grad} \psi + \bar{C}_i v \quad (4-4)$$

Every mole of the species  $i$  carries the electric charge  $z_i F$ , where  $F$  is the faraday. The net electric current density  $I$  (net charge transfer per unit time per unit cross section of the material) is

$$I = F \sum_i z_i J_i \quad (4-5)$$

Conservation of electroneutrality requires that the electric charges of



all species balance one another everywhere in the system

$$\sum_i z_i \bar{C}_i \pm \omega \bar{A} = 0 \quad (4-6)$$

where  $\bar{A}$  is the concentration of fixed charges and  $\omega$  the sign of the fixed charges.

The rate of motion  $v$  of the center of gravity of the pore liquid (convection rate) is proportional to the force with which the electric field acts on a volume element of the pore liquid. The proportionality factor is by definition, the reciprocal of the specific flow resistance of the material  $\rho_o$ . The electric surplus charge per unit volume of the pore liquid excluding the solid matrix, is  $\frac{\omega F \bar{A}}{\epsilon}$  where  $\epsilon$  is the pore fraction.

Thus the convection rate is

$$v = \frac{\omega F \bar{A}}{\rho_o \epsilon} \text{ grad } \psi = \omega \bar{u}_o \text{ grad } \psi \quad (4-3a)$$

where  $\bar{u}_o = \frac{F \bar{A}}{\rho_o \epsilon}$  and has dimensions of electrochemical mobility. Combining Equ. 4-4 and 4-3a one gets

$$I = -F (\sum_i z_i^2 \bar{u}_i \bar{C}_i + \bar{u}_o \bar{A}) \text{ grad } \psi \quad (4-7)$$

and from the definition of the specific conductance

$$\bar{K}_{sp} = - \frac{I}{\text{grad } \psi} = F (\sum_i z_i^2 \bar{u}_i \bar{C}_i + \bar{u}_o \bar{A}) \quad (4-8)$$

The second term in Equ. 4-8 is due to the convection conductivity, which can be formally designated by  $\bar{K}_o$ . Thus

$$\frac{\bar{K}_o}{\bar{K}_{sp}} = \frac{\bar{u}_o \bar{A}}{\sum_i z_i^2 \bar{u}_i \bar{C}_i + \bar{u}_o \bar{A}} \quad (4-9)$$

From Equ. 4-9 one can see that the relative importance of convection conductivity increases with the ratio  $\bar{u}_o/\bar{u}_i$ . The quantity  $\bar{u}_o$  is propor-







tional to the flow resistance. Hence convection conductivity is most important in high exchange capacity material with low flow resistance.

The above treatment involves several idealizations, according to Helfferich. The transport phenomena in a porous medium are described in terms of effective mobilities, whereas they may vary considerably from place to place in the system depending on the distance from the charged pore wall. The uniformity of the distribution of the mobile species is another simplifying assumption. Probably more serious than all these idealizations is an implicit assumption in application of Equ. 4-3 to porous media. This equation implies that convection in the absence of any other force, carries all particles in the pore liquid at the same rate. It disregards the fact that exchange of momentum with the pore walls by mechanical or electrical interactions may retard various species to different degrees. "A more refined theory will have to include this effect" concludes Helfferich (1962). It is possible to treat the interactions between the different ions and that between the individual ion and the solid by means of thermodynamics of irreversible processes. This will be done in the next chapter. However, at present a comprehensive theory of electroosmosis is lacking and even the use of the above theory has not been possible because of lack of necessary data.

#### Procedure

At the end of the conductance experiment the solution outlets at the bottom of the conductivity cell were connected to horizontal calibrated, precision-bore, capillary tubes. An air bubble was introduced



in the capillary in such a way that electroosmotic flow through the soil could be measured by its movement. A known current was passed through the soil plug and the displacement of the bubble was followed with time. At a certain time, the experiment was stopped and total displacement of the bubble was measured.

## Results

Knowing the volume displaced and total current passed, electroosmotic flow, per Faraday per  $\text{cm}^2$ , of the plug was determined. This was found to be  $24 \pm 0.5$  moles per Faraday. This includes the free water as well as that transferred along with ions in the form of the hydration shell. In reporting total solvent transferred, it is common to exclude the water of hydration for cation. Since the hydration number of  $\text{Rb}^+$  is 3, three moles of water will be transferred per mole of  $\text{Rb}^+$  and the total electroosmotic flow of solvent per Faraday will be  $21 \pm 0.5$  moles. In most of the membranes made of exchange resins the electroosmotic flow (with water of hydration) is around 5 - 15 moles per Faraday.

## 4. Transport numbers in soil

### Introduction

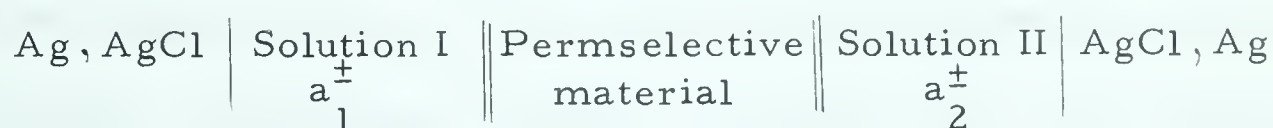
The transference number  $t_i$  of a species  $i$  is defined as the number of moles of the species transferred by 1 Faraday of electricity, through a stationary cross section, in the direction of positive current. This definition is complete only when the frame of reference is specified. The electric current induces convection in ion exchangers and thus it makes a difference whether the solid matrix, solvent or the pore liquid



is considered as stationary. Usually the solid matrix is chosen as the frame of reference and thus the transference of the solvent must also be considered along with that of the cation and anion. Since anions move opposite to the positive direction of the current, their transference numbers would be negative (Scatchard, 1953).

The 'transport number' is defined as the fraction of the electric current carried by the species. The transport number is the product of the transference number and the electrochemical valence of the species.

For a concentration cell of the type



Scatchard (1953) has shown that the resultant e.m.f. can be represented by

$$E = \frac{-RT}{F} \int_I^{II} \left[ \frac{\bar{t}_i}{z_i} d \ln a_i - \frac{\bar{t}_j}{z_j} d \ln a_j + t_w d \ln a_w \right] \quad (1-49)$$

where  $\bar{t}_i$ ,  $\bar{t}_j$  and  $\bar{t}_w$  are the transport numbers of the counter-ion, co-ion and the solvent, and  $a_i$ ,  $a_j$ , and  $a_w$  are the corresponding activities in the solution phase.

If the transport numbers across the permselective membranes can be represented by a single value the above equation can be integrated. The third term on the right hand of Equ. 1-49 can be modified by the Gibbs-Duhem equation

$$d \ln a_w = -0.018 \underline{a_{ij}} d \ln (a_{ij})^2 \quad (4-10)$$

where  $\underline{a_{ij}}$  is the average of molal activities ( $a_{ij}$ ) of the electrolytic







solutions on either side of membrane. Thus Equ. 1-49 becomes

$$\Delta E = -\frac{RT}{F} \left[ \frac{t_i}{z_i} \ln \frac{(a_i)_{II}}{(a_i)_I} - \frac{t_j}{z_j} \ln \frac{(a_j)_{II}}{(a_j)_I} - \bar{t}_w 0.018 \frac{a_{ij}}{(a_{ij})^2_I} \ln \frac{(a_{ij})^2_{II}}{(a_{ij})^2_I} \right] \quad (1-51)$$

where  $\underline{a_{ij}}$  is the average of the two external solution molal activities. For an ideal membrane where  $\bar{t}_i = 1$ , Equ. 1-51 can be written as

$$\Delta E = \left[ \frac{2RT}{F} \frac{\bar{t}_i}{z_i} \ln \frac{(a_{ij})_I}{(a_{ij})_{II}} + \frac{\bar{t}_w RT}{F} 0.018 \frac{a_{ij}}{(a_{ij})^2_{II}} \ln \frac{(a_{ij})^2_I}{(a_{ij})^2_{II}} \right] \quad (4-11)$$

where  $a_{ij}$  is the mean molal activity coefficient in solutions I and II and  $\underline{a_{ij}}$  is the average of these two. If the solutions  $a_{ij}$  are dilute as they are in the present experiment it will be subsequently shown that in spite of the rather high value of  $\bar{t}_w$  (the moles of water transported in the direction of the positive currents per Faraday) the second term on the right hand side of Equ. 4-11 can be neglected. Then Equ. 4-11 for the case of ideal perm-selective membrane, where  $\bar{t}_i = 1$ , becomes

$$\Delta E = \frac{2RT}{F} \ln \frac{(a_{+})_I}{(a_{+})_{II}} \quad (4-12)$$

This is nothing but the Nernst equation and represents the thermodynamically maximum value of the potential possible in an ideal membrane. For nonideal membranes E is less than this value and it is a simple matter to show that

$$\frac{\Delta E}{\Delta E_{\max}} = t_i \quad (4-13)$$

## Procedure

The soil was converted to the Rubidium form and was packed carefully in the soil chamber of the cell, as described previously. The



solution chambers were filled with the appropriate RbCl solutions. The solutions used and their activities are listed in table 2. The solution I ( $a_1$ ) was always placed in the left chamber. The ratio of the activities of Solution I ( $a_1$ ) and Solution II ( $a_2$ ) was always equal to 2. The solutions were kept stirred for 24 hours after which the cell was emptied and fresh quantities of identical solution were introduced to ensure establishment of equilibrium at particular activity of solution. After thermal equilibrium was attained the experiment was started.

The temperature recording was done as previously and the cell was maintained at  $25 \pm 0.2^\circ\text{C}$ . The potential drop was measured with time between what was formerly the current carrying electrodes in the solution chambers of the cell. They were freshly prepared whenever the bias potential exceeded 0.1 mv. The Solution I and Solution II of RbCl were such that their mean molal activity ratio was always equal to two. For this case the  $E_{\text{max}}$  then becomes 35.5 mv. After 20 - 24 hours the solution from the end chambers was removed and they were refilled with the same solution and measurements of the e.m.f. against time continued. Once the values of the potential became invariant with time the experiment was stopped and the e.m.f. was noted. This procedure was repeated for four pairs of solutions.

#### Results and discussion

Figure 13 gives the variation of e.m.f. (mv.) against the time (hours) from the beginning of the experiment. The gaps in the graph represent the time required for the thermal equilibrium at  $25.0 \pm 0.2^\circ\text{C}$ .



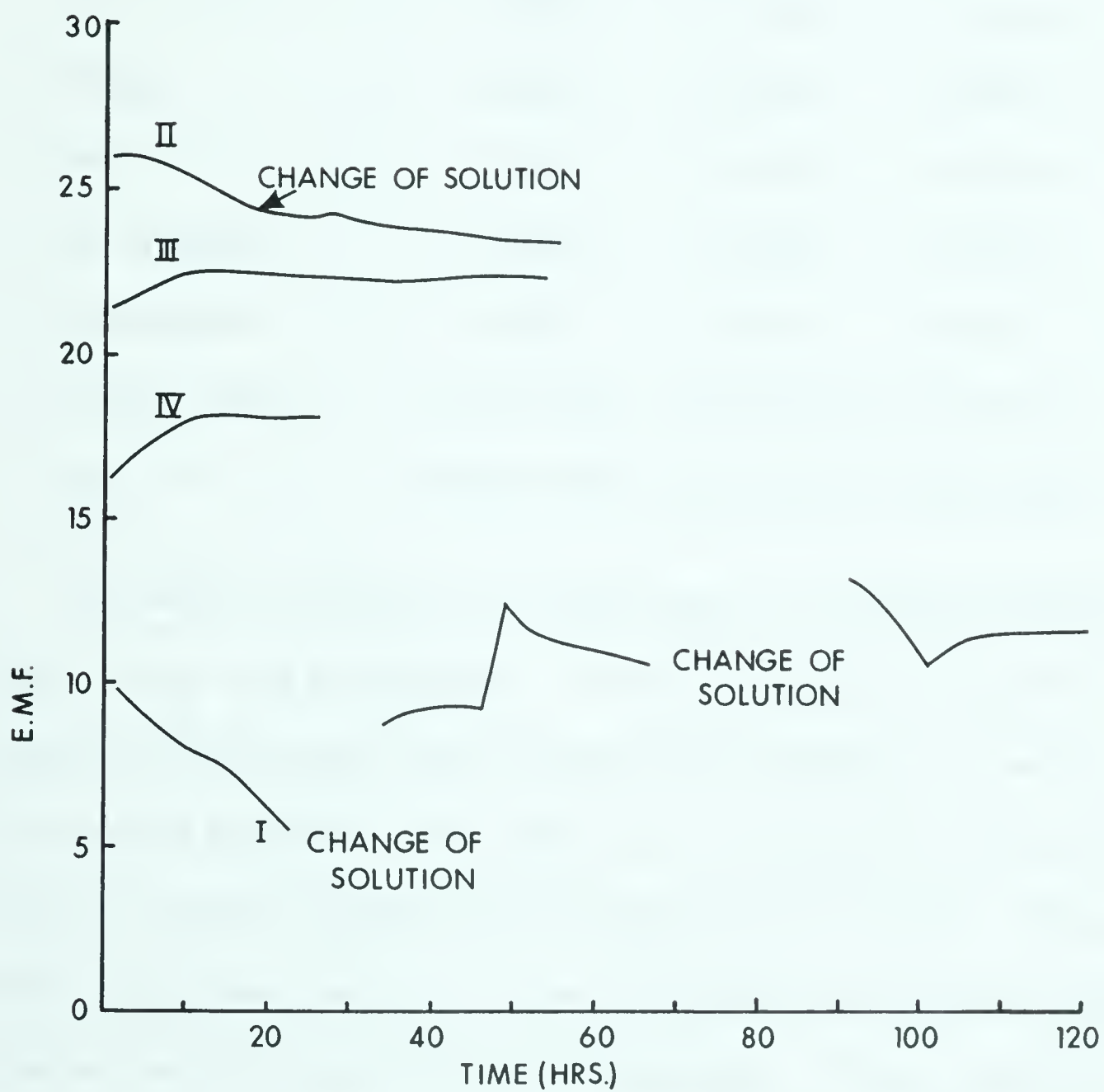


FIG.13 VARIATION OF E.M.F. WITH TIME FOR A CONCENTRATION CELL







Table 12 gives the summary of this series of experiments.

Table 12. Transport numbers in soil at different molal concentrations

| Solution Pair  | I                 | II                | III               | IV                |
|----------------|-------------------|-------------------|-------------------|-------------------|
| $(a\pm)_1$     | 0.0046            | 0.0092            | 0.0184            | 0.0365            |
| $m_1$          | 0.0050            | 0.0102            | 0.0212            | 0.0444            |
| $(a\pm)_2$     | 0.0024            | 0.0046            | 0.0092            | 0.0184            |
| $m_2$          | 0.0025            | 0.0050            | 0.0102            | 0.0213            |
| Average $a\pm$ | 0.0035            | 0.0069            | 0.0139            | 0.0274            |
| Average $m$    | 0.0038            | 0.0076            | 0.0157            | 0.0328            |
| e.m.f. (mv.)   | $11.69 \pm 0.09$  | $23.54 \pm 0.09$  | $22.36 \pm 0.10$  | $17.66 \pm 0.05$  |
| $t_{Rb}$       | $0.329 \pm 0.003$ | $0.663 \pm 0.003$ | $0.630 \pm 0.003$ | $0.497 \pm 0.003$ |

The above calculations are based upon the assumption that the second term in Equ. 4-11 is negligible. It must be pointed out that the transport numbers are the mean values between the molalities,  $m_1$  and  $m_2$  in the two solution chambers. The value of  $t_w$ , determined as described earlier may be considered applicable for Solution pair II and III. Winger et al. (1956) have shown that  $t_w$  is a linear function of the transport number of counter-ion in the permselective membranes. Thus  $t_w$  would be expected to be different for solution pair I and IV. However, with the available data, the magnitude of the second term in Equ. 4-11 may be determined for II and III. These values are 0.1 and 0.2 mv. respectively, which seems to support the earlier assumption. The errors indicated in Table 12 do not take account of the magnitude of the second term of Equ. 4-11 whenever it is accessible but merely indicate the variation in the e.m.f. observed.



It would be safe to consider that since the value of  $t_w$  is likely to be maximum for solution pairs II and III, the magnitude of the second term for the other treatments would be less than 0.2 mv and thus this would represent the maximum error in accuracy of the above measurements.

A modified form of the Hittorf method was tried earlier where the solution in one of the compartments (anode) was tagged with  $\text{Rb}^{86}$  to known specific activity. The amount of  $\text{Rb}^+$  transferred after the passage of known current was determined from the radioactive assay of the solution in the cathode and anode chambers. With this technique the current density and the time required to bring about detectable transfer of radioactive species was considerably reduced. Still the e.m.f. method described above was found to be the best for determinations of transport number due to the minimum currents passed through the soil plugs.

Barrer et al. (1960) have made use of an equation similar to Equ. 4-11, to determine the transport numbers through zeolite membranes. Figure 14 shows the relation between the transport number of the  $\text{Rb}^+$  through the soil plug and the molality of the equilibrated solution phase. Between the molality range of 0.0088 to 0.024 the soil plug behaves as a permselective material with respect to counter-ion since it transfers  $\text{Rb}^+$  preferentially. However, below this molality it seems to become permselective with respect to co-ions as the transport number of  $\text{Rb}^+$  reaches 0.33. The sudden decrease in the transport number in the range of molality of 0.008 to 0.004 also corresponds to the sudden decrease of mean activity coefficient in the soil phase (Fig. 2, chapter 2). Thus the high electrostatic



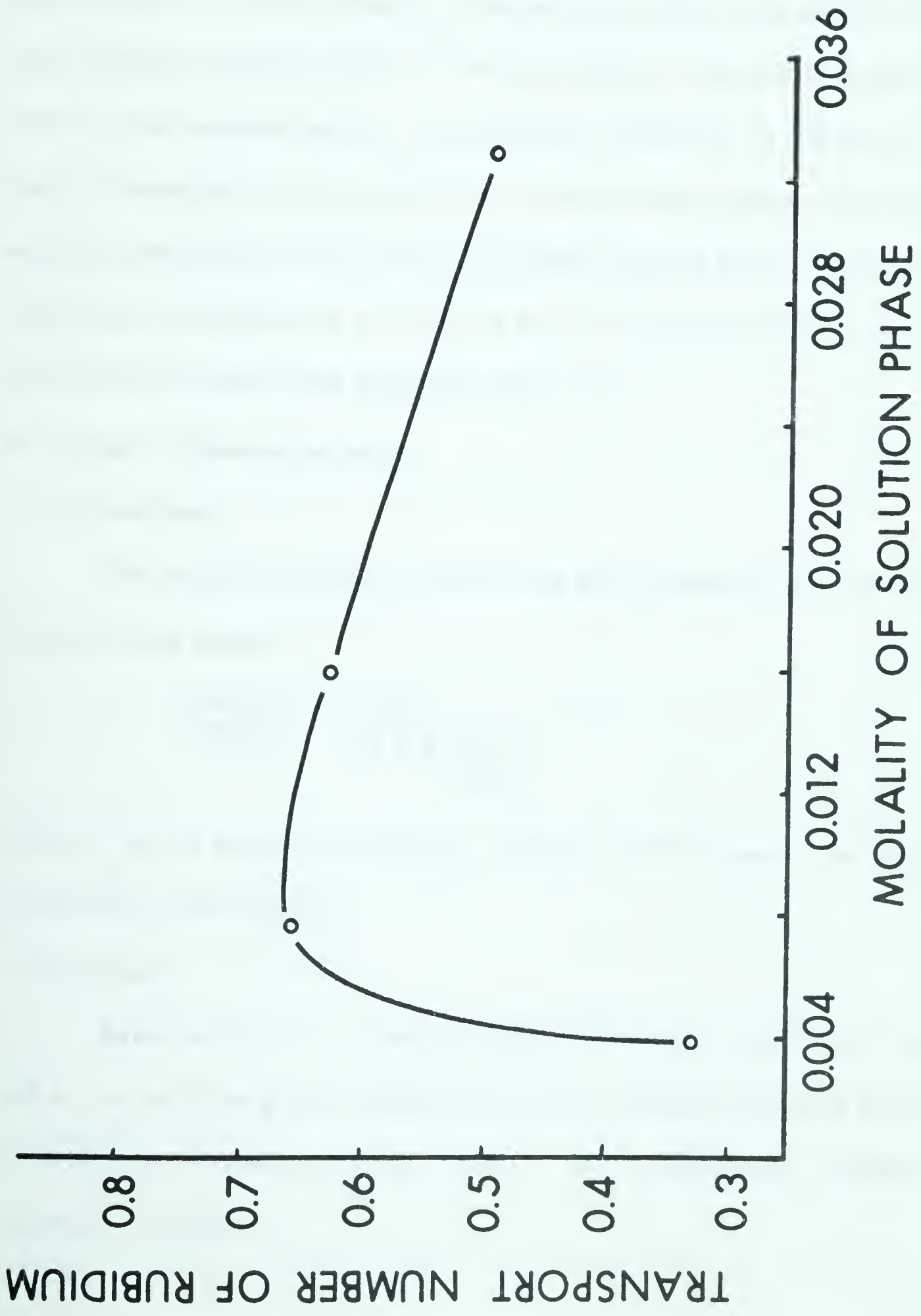


FIG. 14 TRANSPORT NUMBER OF RUBIDIUM IN SOIL AS A FUNCTION OF CONCENTRATION OF SOLUTION PHASE







interactions seem to render the counter-ion immobile so that the greater part of the current is carried by the co-ions, which would be much more mobile due to the repulsive forces set up in the vicinity of the charged clay micelle. As the molality of the solution phase increases beyond 0.024, the transport number of  $\text{Rb}^+$  in the soil plug is expected to approach its value in the solution phase, as the specific influence of the soil vanishes due to 'swamping effect'. Had it not been for the sudden decrease of activity coefficient of  $\text{Rb}^+$  in the soil phase beyond the equilibrium solution phase concentration of 0.008 m the soil plugs would have approached the behavior of the ideal membrane ( $t_{\text{Rb}} = 1$ ).

## 5. Nernst - Einstein relation

### Introduction

The Nernst-Einstein relation has been derived for the soil in chapter 1 and reads

$$\frac{10^3 \bar{t}_i \bar{K}_{sp}}{F C_i h \epsilon} = \frac{D_i z F}{RT h \epsilon} \frac{d \ln a_i}{d \ln c_i} = u_i \quad (1-35)$$

where  $u_i$  is the electrical mobility ( $\text{cm}^2 \text{sec}^{-1} \text{volt}^{-1}$ ) and other symbols have their usual meaning.

### Procedure

Based on Equ. 1-35 and by means of the data reported in chapters 3 and 4, for solution phase molality of 0.01 (in equilibrium with soil phase) the electrical mobilities for  $\text{Rb}^+$  and  $\text{Cl}^-$  were determined. These are reported in Table 13.



## Results and Discussion

Table 13. Mobilities ( $\text{cm}^2\text{volt}^{-1}\text{sec}^{-1}$ ) of  $\text{Rb}^+$  and  $\text{Cl}^-$  in soil and solution

|               | From<br>Soil Elec.<br>Measurement | From<br>Soil diffusion<br>Measurement | In solution<br>at infinite<br>dilution |
|---------------|-----------------------------------|---------------------------------------|----------------------------------------|
| $\text{Rb}^+$ | $5.64 \times 10^{-4}$             | $7.21 \times 10^{-4}$                 | $8.06 \times 10^{-4}$                  |
| $\text{Cl}^-$ | $4.02 \times 10^{-3}$             | $6.98 \times 10^{-4}$                 | $7.90 \times 10^{-4}$                  |

The mobilities for  $\text{Rb}^+$  and  $\text{Cl}^-$  for soil determined by electrical and diffusion measurements are reported in table 13. Above results are not in agreement with those of Spiegler and Coryell (1953) and Despic and Hills (1956) who obtain a higher value for mobility determined from electrical measurements on membrane, than that obtained from the diffusion measurements. If the mechanism of ion migration by electrical conduction and by diffusion were the same, the mobility determined would be identical from both measurements. However, in the permselective material electrical conduction is accompanied by electroosmosis which increases the specific conductance of the exchanger material, as explained earlier. This would be reflected by the greater mobility from electrical measurement compared to that from the diffusion measurement. The electrical mobility of  $\text{Rb}^+$  and  $\text{Cl}^-$  in soil is less than the diffusion mobility. This discrepancy could be because of the fact that the tortuosity factor 'h' obtained from the diffusion measurements was considered applicable to electrical measurements in soil. However, if this factor is  $h^2$  as found by Fatt (1959) in his electrical measurements the corresponding values of mobility for  $\text{Rb}^+$  and  $\text{Cl}^-$  is  $2.66 \times 10^{-3}$  and  $1.88 \times 10^{-2}$



respectively. These values appear reasonable enough, in view of the large electroosmotic flow through the soil plug reported earlier. The ratio of electrical mobilities of  $\text{Rb}^+$  and  $\text{Cl}^-$  is 0.14. The greater electrical mobility of  $\text{Cl}^-$  in the soil compared to that of  $\text{Rb}^+$  also confirms the presence of repulsive forces set up in the range of concentrations of solutions when the soil plug behaves as permselective. This ratio of  $\frac{u_{\text{Rb}}}{u_{\text{Cl}}}$  would later on be compared with the same found out by the graphical procedure outlined by Meyer and Sievers (1936).





## Chapter 5.

### THERMODYNAMICS OF IRREVERSIBLE PROCESSES

#### 1. Need for the use of thermodynamics of irreversible processes

Classical thermodynamics deals exclusively with equilibrium states. It accepts no substitute or approximation to the equilibrium states and the reversible transitions between them. Reversible transitions occur through a continuous set of equilibrium states by processes which occur infinitely slowly and can be reversed by an infinitely small change in the variables which determine the nature of the system. Quasi-thermodynamics which deals with instantaneous states not far from equilibrium differ from classical thermodynamics in conceding that the steady state properties on a microscope scale exist in macroscopic system that is not in equilibrium. "Although this is probably an approximation which is never strictly true, but is better, the closer the system is to equilibrium, it is difficult to imagine science which is not based on it" (Scatchard, 1956). The thermodynamics of irreversible processes, while treating non-equilibrium states like quasi-thermodynamics, allows the nonisothermal conditions to be dealt with unlike the latter. Thermodynamics of irreversible processes which is often called non-equilibrium thermodynamics provides a general framework for the macroscopic description of irreversible processes. In treating the non-equilibrium situation one has to treat basic theory such as this in a way that will take cognizance of the microscopic (local) quantities, since the state variables are continuous functions of space coordinates and time. In equilibrium thermodynamics such local



formulations are unnecessary as the state variables are usually independent of the space and time coordinates.

In soil systems which are basically anisotropic in nature, the coupling of fluxes would be expected to be the rule. Study of these systems on the assumption of isothermal condition may at times be an oversimplification and superimposing of thermal gradients are to be expected on all transport processes in most of the natural soils. Recently Taylor and Cary (1964) have made use of non-equilibrium thermodynamics to study water flow in soil. A comprehensive treatment of transport processes in soil, it would seem, can only be given by the use of non-equilibrium thermodynamics, which allows the elucidation of many cross-effects between different phenomena, such as flux of an ionic species caused by the presence of a chemical potential gradient of that species, as well as thermal gradient.

## 2. Its theory and the phenomenological coefficients

The structure of non-equilibrium thermodynamics is based on the concept of entropy. In the following few pages the main concepts of the theory will be presented as expounded in the monographs by de Groot (1951), de Groot and Mazur (1962) and Tyrrell (1961).

For any macroscopic system, according to the classical thermodynamics the variation of a state function  $S$ , the entropy of the system may be represented by

$$dS = d_e S + d_i S \quad (5-1)$$

where  $d_e S$  is the entropy supplied to the system by its surroundings and



$d_i S$  the entropy produced inside the system. The second law of thermodynamics states that  $d_i S$  must be zero for reversible (equilibrium) transformation and positive for irreversible transformation of the system

$$d_i S \geq 0 \quad (5-2)$$

The entropy supplied  $d_e S$  on the other hand may be positive, zero or negative, depending on the interactions of the system with its surroundings. Thus for an adiabatically insulated system (i. e. a system which can exchange neither heat nor matter with its surroundings)  $d_e S$  is equal to zero and it follows from Equ. 5-1 and 5-2 that

$$dS \geq 0 \quad (\text{for an adiabatically insulated system}) \quad (5-3)$$

This is the well known form of the second law of thermodynamics.

For a so-called closed system, which may only exchange heat with its surroundings, according to the theorem of Carnot-Clausius

$$d_e S = \frac{dQ}{T} \quad (5-4)$$

where  $dQ$  is the heat supplied to the system by its surroundings and  $T$  the absolute temperature at which heat is received by the system.

Thus,

$$dS \geq \frac{dQ}{T} \quad \text{for a closed system} \quad (5-5)$$

which is also a form of second law of thermodynamics.

In thermodynamics of irreversible processes one of the important objectives is to relate the quantity  $d_i S$ , the entropy production, to the various irreversible phenomena which may occur inside the system. It is usual to write Equ. 5-1 and 5-2 in a form which is more suitable for







the description of systems in which the densities of the extensive properties (such as mass and energy) are continuous functions of space coordinates (de Groot and Mazur, 1962).

$$S = \int^V P_s dV \quad (5-6)$$

$$d_e S = \int^\pi J_{s.tot} \cdot d\pi \quad (5-7)$$

$$\frac{d_i S}{dt} = \int^V \sigma dV \quad (5-8)$$

where  $S$  is the entropy per mass unit  $J_{s.tot}$ , the total entropy flow per unit area and unit time,  $\pi$  the surface, and  $\sigma$  the entropy source strength or entropy production per unit volume and unit time. Equation 5-7 is a surface integral, both  $J_{s.tot}$ , and  $d\pi$  being vector quantities, the latter with magnitude  $d\pi$  normal to the surface.

In classical thermodynamics, entropy per unit mass, is for a system in equilibrium, a well-defined function of the various parameters which are necessary to define the macroscopic state of the system completely. In general

$$S = f(U, V, m) \quad (5-9)$$

where  $U$  is the internal energy,  $V$  the volume and  $m$  the concentration. Equ. 5-9 is set out in Gibb's equation.

$$Tds = dU + PdV - \sum_{i=1}^n \mu_i dm_i \quad (5-10)$$

where  $\mu_i$  is the chemical potential of the species

Non-equilibrium thermodynamics rests on two hypotheses, one of which has been mentioned already, viz, that the entropy production is positive; the other fundamental assumption being the validity of Gibb's



equation, implying explicit dependence of entropy  $S$  on energy, volume and concentration. It is assumed that although the total system is not in equilibrium, there exists within small mass elements a state of local equilibrium for which the local entropy  $S$  is the same function (Equ. 5-9) of  $U$ ,  $V$ , and  $m$  as in real equilibrium. In particular it is assumed that Equ. 5-10 is valid for the motion of center of gravity of a mass element.

$$T \frac{dS}{dt} = \frac{dU}{dt} + P \frac{dV}{dt} - \sum_{i=1}^n \mu_i \frac{dm_i}{dt} \quad (5-11)$$

"This hypothesis of 'local' equilibrium can from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it" (de Groot and Mazur, 1962). For most of the familiar transport phenomena, where the deviations from equilibrium are not too great Equ. 5-11 is justified.

By making use of principles of conservation of energy and conservation of mass to substitute for  $\frac{dV}{dt}$  and  $\frac{dm_i}{dt}$  in Equ. 5-11 it can be shown that the entropy source can be expressed as the sum of products of suitably chosen generalized forces ( $X_i$ ) and the flows ( $J_i$ ) caused by these forces. A quantity  $\Phi$  dissipation function can be defined as

$$\Phi = T \, d_i S / dt = \sum_{k=1}^n J_k X_k \quad (5-12)$$

The forces ( $X_k$ ) can be gradients of temperature, chemical potential, electrical potential, etc., to which correspond the heat, diffusion and current flows respectively.

The determination of dissipation function by itself is of little use unless certain phenomenological concepts are combined with it.



It is known empirically that for a large class of irreversible phenomena and under a wide range of experimental conditions the irreversible flows are linear functions of thermodynamic forces. Temperature gradient, concentration gradient and electrical potential gradients as described earlier are called thermodynamic forces in non-equilibrium thermodynamics although they are not forces in the Newtonian sense. Some of the linear phenomenological laws are as follows. Fouriers law for heat conduction states that the components of the heat flow are linear functions of the components of the temperature gradient. Fick's law establishes a linear relation between the diffusion flow of matter and the concentration gradient. Newton's law establishes similar relation between shearing force and velocity gradient, Ohm's law between electrical current and potential gradient, and the chemical reaction law between reaction rate of chemical potentials. These linear phenomenological laws also include flows caused by the action of more than one thermodynamic force. Among such phenomena are, thermoelectricity by the action of thermal and electrical gradients, the Peltier effect (evolution or absorption of heat at junctions of metals resulting from the flow of an electrical current), Soret effect (coupling of diffusion and heat conduction) and Dufour effect (temperature difference arising when a concentration difference exists).

It is possible that some irreversible processes follow non-linear phenomenological laws. However, even for such processes one may assume the linear relations to be valid within a very limited range close to equilibrium. Most of the transport processes however, are linear even







under most extreme experimental conditions.

Thus one can express a general phenomenological law by

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (5-13)$$

where  $J_i$  and  $X_i$  are any of the cartesian components of the independent fluxes and thermodynamic forces appearing in Equ. 5-12. The coefficients  $L_{ii}$  are related to coefficients of thermal, electrical conductivity or diffusion, while those of the form  $L_{ik}$  reflect the effect of force  $X_k$  upon flow  $J_i$ . The phenomenological coefficients  $L_{ik}$  are independent of the process but not necessarily independent of the concentration. For example in a system in which a gradient of chemical potential  $X_i$ , co-exists with a thermal gradient  $X_g$ , the extended phenomenological equation becomes (Tyrrell, 1961)

$$\text{Flow of material} = J_i = L_{ii}X_i + L_{ig}X_g \quad (5-14)$$

$$\text{Flow of heat} = J_g = L_{gi}X_i + L_{gg}X_g$$

The coefficient  $L_{ig}$  is the measure of thermal gradient on diffusion flow and  $L_{gi}$ , that of chemical potential gradient on the heat flow. Since the dissipation function can be expressed as a sum of products of suitably chosen forces and fluxes (Equ. 5-12) and if the linear phenomenological relations are assumed to be true then  $\Phi$  becomes a quadratic function of the forces operating in the system.

$$\Phi = \sum L_{ik} X_i X_k \quad (5-15)$$

Since  $\Phi \geq 0$ , must always be positive or at least non-negative, the coefficients  $L_{ik}$  must satisfy certain conditions. A sufficient condition for this is that all principal cofactors of the symmetric matrix with elements



$L_{ik}$  be positive. All diagonal elements must be positive and all off-diagonal elements must satisfy a certain condition. For example the sufficient condition for  $\Phi \geq 0$  in Equ. 5-14 is  $L_{ii} \geq 0$ ,  $L_{gg} \geq 0$  and that  $L_{ii}L_{gg} - L_{ig}L_{gi} \geq 0$ . The first two conditions are trivial and simply state diffusion coefficient and the coefficient of thermal conductivity are positive. The third is more important in that it sets the upper limit to the size of the cross coefficient.

The most fundamental theorem in non-equilibrium thermodynamics as set forth by Onsager (1931) is that

"Provided a proper choice is made for the 'fluxes'  $J_i$  and 'forces'  $X_i$  the matrix of phenomenological coefficients  $L_{ik}$  is symmetric".

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, n) \quad (5-16)$$

Equation 5-16, the Onsager reciprocal relation proved by the principle of microscopic reversibility is central to the theory of irreversible processes. Microscopic reversibility postulates symmetry of all mechanical equations of motion of individual particles with respect to the time  $t$ , or in other words, the invariance under the transformation  $t \rightarrow -t$ . This is true for classical as well as for quantum mechanical equations of motions. In Onsager's derivation no assumptions of the transport phenomena are made, the result being generally valid for an arbitrary process. Although the Onsager theorem rests on ideas about microscopic behavior of physical systems, the result is macroscopic.

Consider the dissipation function

$$\Phi = J_1X_1 + J_2X_2 + J_3X_3 \quad (5-17)$$



where  $X_1$ ,  $X_2$ , and  $X_3$  are the thermodynamic forces applied to a cation, anion and solvent species,  $J_i$ 's being the corresponding flows. On the assumption of linearity of the phenomenological laws, one then gets for fluxes:

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \\ J_2 &= L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \\ J_3 &= L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \end{aligned} \quad (5-18)$$

where fluxes were considered as dependent variables. If the forces are considered dependent Equ. 5-18 may be written as

$$\begin{aligned} X_1 &= R_{11}J_1 + R_{12}J_2 + R_{13}J_3 \\ X_2 &= R_{21}J_1 + R_{22}J_2 + R_{23}J_3 \\ X_3 &= R_{31}J_1 + R_{32}J_2 + R_{33}J_3 \end{aligned} \quad (5-19)$$

where  $L_{ij}$  and  $R_{ij}$  correspond to admittance and resistance matrices, for both of which Onsager reciprocal relations are held equally valid.

$R_{ij}$ 's are connected to  $L_{ij}$ 's by

$$R_{ij} = \frac{A_{ij}}{L} \quad (5-20)$$

$A_{ij}$  being the minor of  $L_{ij}$  and  $L$ , the determinant of  $L_{ij}$ 's. In a similar manner.

$$L_{ij} = \frac{B_{ij}}{R} \quad (5-21)$$

where  $B_{ij}$  is the minor of  $R_{ij}$  in the determinant  $R$ .

Staverman (1951, 1952) was first to apply the thermodynamics of irreversible processes to transport phenomena across membranes. He





showed how these were related to the coefficients  $L_{ik}$ 's. There are  $n(n+1)/2$  of these coefficients if there are  $n$  components since  $L_{ik} = L_{ki}$  according to Onsager's reciprocal theorem. In order to estimate all  $L_{ik}$  from the measurements of fluxes under known thermodynamic forces,  $n(n-1)$  independent measurements are needed. For a system consisting of 3 components (e.g. cation, anion, and water) as in Equ. 5-18, 6 independent measurements are necessary. Lorimer et al. (1956) have shown how some of these relationships can be obtained.

For solution of electrolytes Equ. 5-13 becomes

$$J_i = C_i v_i = \sum_{k=1}^n L_{ik} X_k \quad (5-22)$$

$$\text{where } X_k = z_k F \text{ grad } \psi + (\text{grad } \mu_k)_t \quad (5-23)$$

$C_i$  being molal concentrations and  $v_i$  the velocity and  $\psi$  the electrical potential.

The mobility  $u_i$  ( $\text{cm}^2 \text{sec}^{-1} \text{volt}^{-1}$ ) is given by

$$u_i = \left| \frac{v_i}{- \text{grad } \psi} \right|_{T, \mu_k} = \frac{F}{C_i} \sum_{k=1}^n L_{ik} z_k \quad (5-24)$$

The total current  $I$  is given by:

$$I = \sum_{i=1}^n z_i F J_i = \sum_{i=1}^n z_i F \sum_{k=1}^n z_k F L_{ik} \text{ grad } \psi \quad (5-25)$$

Current carried by species  $i$  is

$$z_i F J_i = z_i F \sum_{k=1}^n z_k F L_{ik} \text{ grad } \psi \quad (5-26)$$

So the transport number of species  $i$ , (i.e. the fraction of the total current carried) can be represented by:

$$t_i = \frac{z_i F J_i}{\sum_{i=1}^n z_i F J_i} = \frac{z_i F \sum_{k=1}^n z_k F L_{ik}}{\sum_{i=1}^n z_i F \sum_{k=1}^n z_k F L_{ik}} \quad (5-27)$$



The specific conductance can be represented by

$$K_{sp} = \sum_{i=1}^n z_i F \sum_{k=1}^n z_k F L_{ik} \quad (5-28)$$

### 3. Spiegler's friction model

Spiegler (1958) has introduced a friction model in treating the flow of a cation, an anion and water through a permselective porous plug. Here the phenomenological laws are set out in terms of friction coefficient  $G_{ik}$ 's instead of the  $L_{ik}$ 's. The two of necessity will be related but the friction model has two advantages:

- (i) It is hoped that  $G_{ik}$ 's may be less concentration dependent compared to  $L_{ik}$ 's.
- (ii) The calculation performed with  $G_{ik}$  coefficients are simpler and it is possible to associate simple physical meaning with them.

The fluxes of mobile species in an ionic porous plug such as soil would be given by Equ. 5-18 where the fact that the fluxes are the result of interaction of all the forces is taken account of. Equation 5-18 thus relates the fluxes of cation (subscript 1), anion (2) and water (3) to the forces applied to them. The ultimate aim of the study of transport processes in soil is to predict the fluxes knowing the forces or vice versa. At present most of the provinces in Canada maintain soil testing laboratories which provide guidance to the farmers on the extent of fertilizing of their crops based on chemical examination of their soil samples. If the phenomenological coefficients  $L_{ik}$  are obtained for natural undisturbed cores then it is possible to assess the



fertilizer needs much more accurately and predict the approximate fluxes for the plant nutrients involved. A given set of  $L_{ik}$  coefficients apply only to a particular system of porous medium and solution. If the properties of the system change these would not hold true. It is necessary to know the magnitude of 6 coefficients from Equ. 5-18 since three of the total of 6 phenomenological equations are equal by Onsager reciprocal relations. In principle six independent measurements are required in order to determine the six phenomenological coefficients. If some interactions are negligible, the number of independent variables could be reduced.

#### 4. Friction coefficients and phenomenological coefficients in soil

The model (Fig. 15) used by Spiegler is represented by the sodium (1) and chloride (2) ions (along with their water of hydration) as small bodies in contact with water (3) and with the solid walls of the pores (4). In ion exchange resin (4) represents the polymer network, whereas in soil it would represent the clay micelle forming the periphery of the pore. A force, such as an electrical potential would cause ionic migration in such a system. If the motion of the ions were unhampered they would accelerate continuously and acquire very high linear velocities. However, with dynamic equilibrium, set up almost instantly the force on the ions is counterbalanced by the friction forces, and the ions migrate at constant linear velocity. In this model friction is represented as if the particles were macroscopic. "Of course, for small particles such as ions, the macroscopic concept of friction makes little sense. The hindrance of the







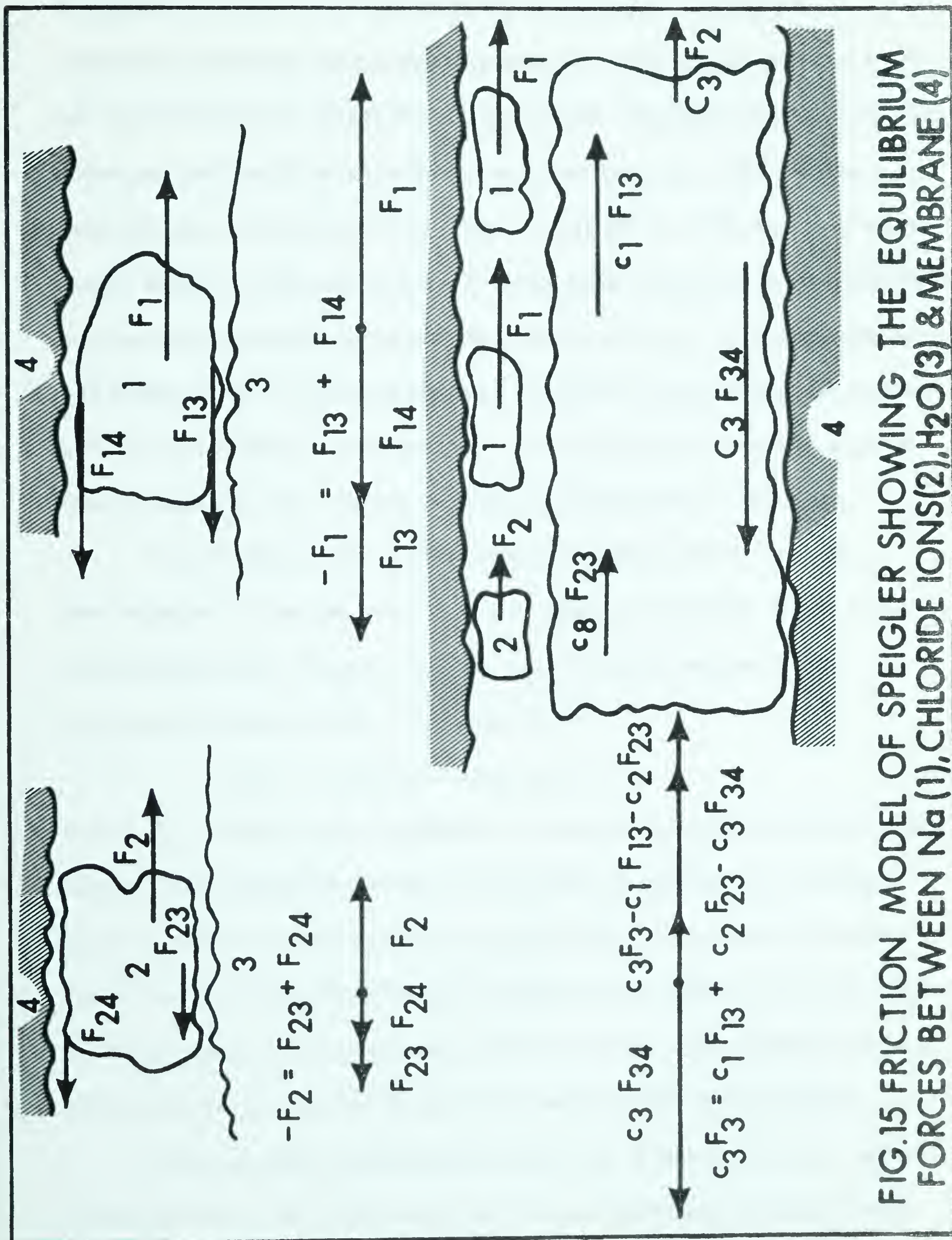


FIG.15 FRICTION MODEL OF SPEIGLER SHOWING THE EQUILIBRIUM FORCES BETWEEN Na(1),CHLORIDE IONS(2),H<sub>2</sub>O(3) & MEMBRANE (4)



straight-line motion of an ion is to be envisaged as a multitude of collisions with other particles, in particular water molecules and atoms of the solid matrix" (Spiegler, 1958). These collisions force the ion into a devious path and thus slow down its linear velocity. The "linear velocity" as used here is an average, irrespective of the tortuous microscopic motions of the particles. It is the time required for the particle to traverse the macroscopic dimensions of the plug. In this treatment one single property is assumed to be common to the hypothetical friction and the true collision processes; that is if a force is applied to a given type of particle its linear velocity is proportional to the force.

The simple law of friction states that the friction force  $X_{13}$  that impedes the motion of an object (1) gliding on another object (3) is proportional to the relative velocity  $u_{13}$  of (1) with respect to (3), provided the interfaces are well lubricated.

$$X_{13} = -G_{13}u_{13} = -G_{13}(u_1 - u_3) \quad (5-29)$$

where  $G_{13}$  is the friction coefficient between the objects (1) and (3). The negative sign indicates that the friction force operates in a direction opposite to the velocity of the moving particle. With force in wattsec  $\text{cm}^{-1} \text{mole}^{-1}$ , the units of friction coefficient are watt sec sec  $\text{cm}^{-2} \text{mole}^{-1}$ . The force and friction coefficient refer to one mole of mobile particle (1) and the interaction of this amount with particles (3) in its vicinity.

In the system consisting of sodium (1), chloride (2) ions, water (3) and an ionic solid matrix (4), six friction processes between these components are possible. They are  $G_{12}$ ,  $G_{13}$ ,  $G_{14}$ ,  $G_{23}$ ,  $G_{24}$ ,  $G_{34}$ .





Spiegler derived complete flux equation for this model expressing the L-coefficients in Equ. 5-18 in terms of concentrations of the mobile particles and of these friction coefficients. However, with a simplifying assumption that because of the co-ion exclusion from a cation exchange porous plug (or membrane), the concentration of co-ion being very small in comparison to the counter-ion, the friction between cation and anion was neglected.

With the vectorial addition of forces  $X_1$ ,  $X_2$ , and  $X_3$  and the friction forces  $X_{13}$ ,  $X_{14}$ ,  $X_{23}$ ,  $X_{24}$ ,  $X_{34}$  (Fig. 15), following relations were arrived at (Fig. 15 is the original diagram (Spiegler, 1955) where  $(F)$  corresponds to  $(X)$  in present treatment.)

$$X_1 = -(X_{13} + X_{14}) = G_{13}(u_1 - u_3) + G_{14}u_1 \quad (5-30)$$

$$X_2 = -(X_{23} + X_{24}) = G_{23}(u_2 - u_3) + G_{24}u_2 \quad (5-31)$$

$$X_3 = \frac{C_1}{C_3}X_{13} + \frac{C_2}{C_3}X_{23} - X_{34} = \frac{C_1}{C_3}G_{13}(u_3 - u_1) + \frac{C_2}{C_3}G_{23}(u_3 - u_2) + G_{34}u_3 \quad (5-32)$$

In Equ. 5-30 the force  $X_1$  applied to one mole of cation is balanced against friction forces  $X_{13}$  and  $X_{14}$  which oppose the motion of cation and have therefore negative values (Fig. 15). Equation 5-31 referring to anion is analogous. Equation 5-32 is derived from the force equilibrium of 1 ml. of solution. The number of moles of cation, anion and water per ml. are  $C_1$ ,  $C_2$ , and  $C_3$  respectively. Hence the forces acting in the positive direction are  $C_3X_3$ ,  $-C_1X_{13}$ , and  $-C_2X_{23}$ . These are opposed by the friction force  $C_3X_{34}$  which has a negative sign.





Equations 5-30 to 5-32 are solved for velocities  $u_i$ . Then each velocity is multiplied by the corresponding concentration to yield flux

$$J_i = C_i u_i \quad (5-33)$$

The result is a set of equations like 5-18 with the following values of L-coefficients-in terms of G-coefficients.

$$\begin{aligned} L_{11} &= (C_1/d) \left[ (C_1 G_{13} + C_3 G_{34}) (G_{23} + G_{24}) + C_2 G_{23} G_{24} \right]; \\ L_{22} &= (C_2/d) \left[ (C_2 G_{23} + C_3 G_{34}) (G_{13} + G_{14}) + C_1 G_{13} G_{14} \right]; \\ L_{12} &= L_{21} = \left( \frac{C_1 C_2}{d} G_{13} G_{23} \right); \quad L_{23} = L_{32} = \left( \frac{C_2 C_3}{d} (G_{13} + G_{14}) G_{23} \right); \\ L_{13} &= L_{31} = \left( \frac{C_1 C_3}{d} G_{13} (G_{23} + G_{24}) \right); \quad L_{33} = \left( \frac{C_3^2}{d} (G_{13} + G_{14}) (G_{23} + G_{24}) \right); \end{aligned} \quad (5-34)$$

where  $d$  is defined as

$$d = C_1 G_{13} G_{14} (G_{23} + G_{24}) + C_2 G_{23} G_{24} (G_{13} + G_{14}) + C_3 G_{34} (G_{13} G_{14}) (G_{23} + G_{24})$$

It is seen that in the present treatment Onsager reciprocity relations (Equ. 5-16) is obeyed and thus the model employed here does not violate the general laws of the thermodynamics of irreversible processes.

However, this model introduces an additional relation

$$L_{13} L_{23} = L_{12} L_{33} \quad (5-35)$$

In Equ. 5-34 the six independent L-coefficients of the flux equation 5-18 are expressed in terms of the volume concentrations of mobile ions and of water and of five friction parameters, namely  $G_{13}$ ,  $G_{14}$ ,  $G_{23}$ ,  $G_{24}$ , and  $G_{34}$ . The lack of one parameter resulted from the assumption that the frictional interaction between the cations and anions is negligible.

The unique part of Spiegler's treatment lies in determination of



the above five friction coefficients by means of five independent measurements, namely, selfdiffusion, coefficients of cations and anions, ( $D_1$  and  $D_2$ ), electroosmotic flow ( $\Omega$ ), transport number ( $t_1$ ) and the specific conductance measurement ( $K_{sp}$ ). He has been able to express the above parameter in terms of the five friction coefficients listed above.

$$D_1 = \frac{RT}{G_{13} + G_{14}} \quad (5-36)$$

$$D_2 = \frac{RT}{G_{23} + G_{24}} \quad (5-37)$$

$$\Omega = \frac{(FC_3)}{d} C_1 G_{13} (G_{23} + G_{24}) - C_2 G_{23} (G_{13} + G_{14}) \quad (5-38)$$

$$K_{sp} = (F^2/d) C_1 (G_{23} + G_{24}) (C_1 G_{13} + C_3 G_{34}) + C_2 (G_{13} + G_{14}) (C_2 G_{23} + C_3 G_{34}) + C_1 C_2 (G_{23} G_{24} - 2G_{13} G_{23} + G_{13} G_{14}) \quad (5-39)$$

$$t^+ = \frac{(F^2 C_1)}{K_{sp} d} (C_1 G_{13} + C_3 G_{34}) (G_{23} + G_{24}) + C_2 (G_{23} G_{24} - G_{13} G_{23}) \quad (5-40)$$

Thus the measurable quantities  $D_1$ ,  $D_2$ ,  $\Omega$ ,  $K_{sp}$ ,  $t^+$  have been related to  $G_{ik}$ 's. It can be shown that Equ. 5-36 to 5-40 can be solved for  $G_{ik}$ 's and therefrom by Equ. 5-34 the phenomenological coefficients can be determined, by measurements of the selfdiffusion coefficients of the two mobile ions, water transport, conductance and transport number. The volume concentrations of the mobile ions,  $C_1$ ,  $C_2$  and  $C_3$  of water in the porous media must be known. It is important that none of these measurements involve the application of pressure and that they all can be carried out in the absence of a concentration gradient across the membrane. This relatively simple treatment is only possible if no concentration gradients occur. If



this is the case  $G_{ik}$  must be averaged over the concentration.

Assuming that the model postulated by Spiegler holds for a soil plug, the friction coefficients  $G_{ik}$ 's and from those the phenomenological coefficients  $L_{ik}$ 's in Equ. 5-22 were determined\* from the self-diffusion measurements of  $\text{Rb}^+$  and  $\text{Cl}^-$ , transport number, conductance and electroosmotic flow measurements. The above measurements have already been reported in the previous two chapters. Spiegler recognized that his treatment of transport processes in ionic membranes by the friction model was at best an approximate one. The interactions between cation, anion and water, and between these and the solid matrix are much more complex. The model essentially excludes the systems that develop the double layers on the surface. For the systems which develop the electric double layers, friction coefficients such as  $G_{14}$  and  $G_{24}$  would appear rather naive indeed.

For a clay system where the electric double layers are formed, it is probable that the physical contact between the migrating cation and the solid matrix of the clay occurs very seldom and, it is very likely that the friction coefficient that is operative here is  $G_{11}$  rather than  $G_{14}$ . This would however depend on the contribution of the cations from the double layer (soil phase) to the total migration of the species. However, in the soil porous plug there is considerable portion of the solid matrix that is not charged as the clay content of the average soil is often less than 30 - 40% of the total solid material. The friction coefficients obtained in the soil system are thus necessarily averages of the interactions of

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\* For calculations of Friction and Phenomenological coefficients see Appendix (section 6).





mobile species (cation, anion, water) with the charged (clay) as well as uncharged (inert sand, silt) solid surfaces.

In spite of the limitations of the model, Spiegler's treatment represents a useful means of associating simpler physical concepts to otherwise rather abstract flux equations. Their value in soil systems would depend on the degree of accuracy with which the equation of type 5-18 with the known values of  $L_{ik}$ 's are able to predict fluxes from known forces or vice versa. In view of the complexities of the transport processes in soils, and particularly because of the numerous forces at work, it would seem that comprehensive treatment employing the principles of thermodynamics of irreversible processes would be indispensable.

Table 14 gives the values of the friction coefficients and the phenomenological coefficients for the soil plug.

Table 14. Friction and Phenomenological coefficients for Soil Plug

| $G_{ik}$ 's ( $\text{Wsec}^2\text{cm}^{-2}\text{mole}^{-1}$ ) | $L_{ik}$ 's ( $\text{mol}^2\text{wattsec}^{-1}\text{sec}^{-1}\text{cm}^{-1}$ ) |
|---------------------------------------------------------------|--------------------------------------------------------------------------------|
| $G_{13} = 2.28 \times 10^{10}$                                | $L_{11} = 3.43 \times 10^{-12}$                                                |
| $G_{14} = -1.90 \times 10^{10}$                               | $L_{12} = -7.82 \times 10^{-17}$                                               |
| $G_{23} = -5.28 \times 10^{10}$                               | $L_{13} = 5.59 \times 10^{-15}$                                                |
| $G_{24} = 5.38 \times 10^{10}$                                | $L_{21} = -7.82 \times 10^{-17}$                                               |
| $G_{34} = 1.40 \times 10^{11}$                                | $L_{22} = 9.71 \times 10^{-15}$                                                |
| $G_{13}^0 = \frac{RT}{D_1^0} = 1.20 \times 10^8$              | $L_{23} = -3.66 \times 10^{-15}$                                               |
| $G_{23}^0 = \frac{RT}{D_2^0} = 1.22 \times 10^8$              | $L_{31} = 5.59 \times 10^{-15}$                                                |
|                                                               | $L_{32} = 3.66 \times 10^{-15}$                                                |
|                                                               | $L_{33} = 2.61 \times 10^{-13}$                                                |



The negative sign of the friction coefficients  $G_{14}$  and  $G_{23}$  would imply that the friction force vector operates in the same direction as the velocity vector of the particle (Equ. 5-29). It would be instructive to compare  $G_{13}$  and  $G_{23}$  with the corresponding coefficients in free solution determined by means of Equ. 5-36 and 5-37 by making use of Nernst limiting values for  $D_1$  and  $D_2$ . Friction coefficient  $G_{13}$  is to be taken as representing friction between one mole of cations and the bulk of water. However, in a unit volume of soil plug the water content is much less, so that a ratio of  $\frac{G_{13}}{\theta}$  (where  $\theta$  is the volumetric moisture content) would refer to the friction of one mole of cations with a unit volume of water. Due to the dilute nature of solution, the apparent molal volume of RbCl in the solution phase can be neglected. Parson (1959) gives the value  $39.092 \frac{\text{cm}^3}{\text{mole}}$  for the apparent molal volume of RbCl in aqueous solution. The value of  $\frac{G_{13}}{\theta}$  and  $\frac{G_{23}}{\theta}$  for the soil plugs are  $3.5 \times 10^{10}$  and  $8.12 \times 10^{10}$ . Comparing these with the values of  $1.20 \times 10^8$  and  $1.22 \times 10^8$ , one can see that the friction for  $\text{Rb}^+$  and  $\text{Cl}^-$  with water is greater in the soil by two orders of magnitude, compared to that in the solution. The greater friction between water and anion compared to water and cation is significant. Normally the coefficient  $G_{12}$  and  $G_{21}$  would reflect the time of relaxation effect. In this model  $G_{12}$  and  $G_{21}$  were considered insignificant because of the negligible concentration of co-ion. This assumption is amply reflected by phenomenological coefficients  $L_{12}$  and  $L_{21}$ , whose values are the least.

The flux equations corresponding to Equ. 5-18 for the soil system





used becomes as follows:

$$\begin{aligned} J_1 &= 3.43 \times 10^{-12} X_1 - 7.82 \times 10^{-17} X_2 + 5.59 \times 10^{-15} X_3 \\ J_2 &= -7.82 \times 10^{-17} X_1 + 9.71 \times 10^{-15} X_2 - 3.66 \times 10^{-15} X_3 \\ J_3 &= 5.59 \times 10^{-15} X_1 - 3.66 \times 10^{-15} X_2 + 2.61 \times 10^{-13} X_3 \end{aligned} \quad (5-41)$$

In the above equation one can see that the force ( $X_2$ ) on the anion would reduce the flux of the cation and vice versa. It will be noticed that the value of  $L_{22}$  is less than that of  $L_{11}$  by three orders of magnitude and is less than that of  $L_{33}$  by two orders of magnitude. This low value of  $L_{22}$  is, however, contrary to the earlier findings. It can be shown that  $L_{22} = \frac{u_2 c_2}{zF}$  and  $L_{11} = \frac{u_1 c_1}{zF}$ . Using the values of  $L_{ij}$  coefficients and the

concentrations of anion and cation, one can determine the mobility ( $\text{cm}^2 \text{volt}^{-1} \text{sec}^{-1}$ ) of the species. These values are  $u_{Cl} = 9.85 \times 10^{-5}$  and  $u_{Rb} = 2.68 \times 10^{-3}$ . In chapter 4, section 5, the mobilities of the  $Rb^+$  and  $Cl^-$  by electrical measurements taking the tortuosity factor as  $h^2$ , was reported to be  $u_{Rb} = 2.66 \times 10^{-3}$  and  $u_{Cl} = 1.88 \times 10^{-2}$ . While the value for cation mobility agrees there is a large discrepancy in that of anion. Thus friction model is to some extent an oversimplification of the forces existing in soil, at least as far as anion migration is concerned.

Perhaps the greatest importance of thermodynamics of irreversible processes for soil lies in investigating the use of Equ. 5-14. Here the effect of chemical potential as well as thermal gradient can be investigated. Another advantage here is the fact that these two are experimentally adjustable and well defined forces.



Chapter 6.

SUMMARY OF RESULTS

It was pointed out that the seat of most of the physico-chemical reactions in inorganic soil is the charged surfaced of the clay particles. In the present treatment these were considered rigid and homogeneously distributed in the solid matrix. In this respect the soil system as treated here resembles the cation exchange resins where the fixed anionic groups are evenly anchored to the polymer network. However, the difference in the two models stems from the multivalent nature of the clay particle where there is a formation of an electric double layer of counterions. Provided the potentials are small enough in the vicinity of the clay particle this double layer thickness is comparable to  $1/\kappa$ , the Debye-Huckel parameter representing the ionic atmosphere. The theory of the electric double layer as postulated by Gouy-Chapman, with subsequent modification by Stern, describes the distribution of ions and the potential in the vicinity of the charged particle. In ion exchange resins, provided the counterions are dissociated completely, the concentration of the pore liquid tends to be fairly uniform. This is especially the case when rigid membranes are involved where the pore space is considerably reduced. In plugs of exchange resins formation of double layers, similar to that formed on clay particles, is expected as a result of higher porosity. However, the electrical potentials produced would not approach those of the clay particles because of the much greater charge density on normal clays. Because of the formation of the electric double layer, clay micelles





represent a number of islands of high concentration of ions dispersed in a solution of much lower concentration. With more than 95 - 99% of the ions within a few angstroms of the clay surface in the diffuse double layer, such systems are in no way homogeneous in this distribution of ionic charge. For this reason, therefore, a clay electrolyte system was treated as a two phase system in the present work.

Usually the concentrations of the counter-ions adsorbed are expressed as moles per kilogram of solution in the pores of the porous plug or membrane. However, the soil plug is a porous medium of considerably higher porosity than membranes, where the diameter of the pores is supposed to be small enough to prevent the formation of the electric double layers. In a soil system expressing the concentration of the counterions on a similar basis would be misleading. In this study the concentration of the cations adsorbed was expressed as moles per kgm. of solid matrix of the soil. Since the dissociated cations are within  $10 - 20 \overset{\circ}{\text{A}}$  of the charge surface, this seems justifiable and the results of this study indicate this forcefully. Because of this distribution of the ionic species, many concepts of electrochemistry need modification when applied to such colloidal systems.

According to Guggenheim, the partial molal free energy of the ionic species is completely defined by the electrochemical potential

$$\frac{(\partial F)}{(\partial n_i)_{P, T}} = \bar{\mu}_i = \mu_{\text{chem}} + zF\psi \quad (2-15)$$

where  $\mu_{\text{chem}}$  is the chemical potential of the species and  $\psi$  is the





electrostatic potential at the point considered. Since the potential in the vicinity of the charged surface varies from point to point, the chemical potential also varies. It must be pointed out that complete separation of the electric potential and the chemical potential is arbitrary so that it is always the sum of the two that is meaningful. Since at equilibrium the partial molal free energy of the ionic species must be the same, the value of  $\bar{\mu}_i$ , the electrochemical potential is invariant in the system. The chemical potential of the solute species must be the same throughout the system; but that for the ionic species varies from point to point as the electrostatic potential varies. Thus on a microscale one would expect the osmotic pressure to vary also. The electrochemical parameters for such clay electrolyte solutions thus represent the geometric averages over the whole system. They do not reveal the information about the details of the double layer. Recently Bolt (1960), and Taylor (1960), have examined these aspects. The criticism has been that since thermodynamic treatments are unable to characterize the double layer, and hence the surface properties, their value for the clay systems is limited. The essential structure of the double layer is adequately if not completely described by the double layer theory of Gouy-Chapman which is non-thermodynamic in character.

The present author agrees with the essential criticism of the above workers. However, the applicability and usefulness of any parameter describing ion-clay particle interactions, whether strictly thermodynamic or not, lies in its explanation of physically observable phenomena. If the



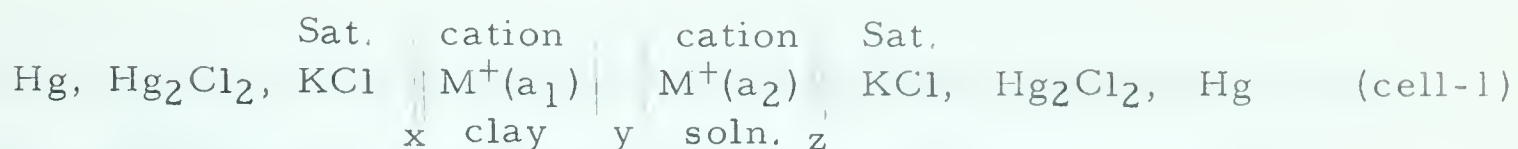
gross averaging of any particular parameter renders it unable to do so, there would be every justification to re-examine its usefulness. In the present work it has been shown that the concept of mean activity coefficient, though outwardly rather nebulous in relation to the clay system, still seems to explain the reduction in the diffusion coefficient of the solute through the soil. The Nernst-Hartley relation, modified to take into account the geometry of the ionic path, was shown to be

$$\bar{D}_{12} = \bar{D}_{12}^0 \left( \frac{\partial \ln \bar{a}_{\pm}}{\partial \ln \bar{m}} \right) h \quad (3-30)$$

where  $\bar{D}_{12}$  is the diffusion coefficient of the solute species (RbCl in this case),  $h$  is the geometry or tortuosity factor (labyrinth factor), and  $\bar{D}_{12}^0$  is the limiting value for the diffusion coefficient of solute as obtained by the Nernst limiting law. It was shown by means of self-diffusion measurements that with the accurate estimation of 'h', the value of  $(\partial \ln \bar{a}_{\pm} / \partial \ln \bar{m})$  corresponds to the value of  $\bar{r}_{\pm}$ , the mean activity coefficient. The value of  $(\partial \ln \bar{a}_{\pm} / \partial \ln \bar{m})$  from diffusion measurements was found to be 0.2382. The value of  $\bar{r}_{\pm}$  obtained independently by the use of Donnan equilibrium was 0.2400. These values agree within  $\pm 0.8\%$ . The factor  $(\partial \ln \bar{a}_{\pm} / \partial \ln \bar{m}_{\pm}) \equiv \partial \bar{a}_{\pm} / \partial \bar{m}_{\pm} \equiv \bar{r}_{\pm}$  if  $\bar{r}_{\pm}$  is constant for a certain range of molality change. Gast (1962) has shown that in the corresponding equation  $\bar{D}_i = D_i^0 \bar{r} h$  for a single ionic species, the parameter  $\bar{r}$  corresponds to the 'fraction active' of Marshall (1951). The fraction active is the ratio of the electrochemically measured activity to the total concentration of the ion concerned. Fraction active is thus analogous to the single ion activity coefficient measured by the concentration cell







where y is the clay membrane electrodes reversible with respect to the particular cation in question. The presence of a liquid junction potential has often been postulated at junction x. However, recently the evidence of negligible junction potential in similar colloidal and polyelectrolyte systems is accumulating. Since in the present work the findings of Gast with regard to single ion activity coefficients were established by purely thermodynamic means it is felt that the single ion activities and mean molal activities of ions in the soil system, in spite of being gross geometric averages, offer a tangible explanation of the physical forces at work, and are experimentally determinable and well-defined quantities for a particular system.

In self-diffusion studies in soil plugs with depleted solution phase (depleted by the application of external pressure), the contribution of the double layer cation to the total migration is increased until at 15 atmospheres most of the cation transport was through these double layers. The activation energies for such surface migration were approximately 1/3 of those found for the saturated soil plugs where the solution phase occupied all the porespace and where probably most of the transport took place through the solution phase. The activation energy of diffusion for  $\text{Cl}^-$  was initially the same as that for  $\text{Rb}^+$  but increased considerably with the removal of solution by external pressure. Here the  $\text{Cl}^-$  in the thin films of solution are increasingly subjected to the fields of the double layer where the counterions must form intense clouds around them. Thus



while the activation energies of diffusion for the cation decreased, those for the anion increased. The evidence of increase in the entropy for diffusion also points to the massive interaction of the cations with the charged surfaces and solvent molecules.

The transport number data show that the soil plug becomes permselective with respect to the cation in the range of solution phase concentrations of 0.0080 - 0.0160 molal. Below 0.0080 molal there is a change in permselectivity from that of cation to anion. This region of change-over corresponds also to the sharp drop in the mean activity coefficient in the soil phase. Fig. 16 shows the plot of e.m.f. vs. the  $\log 1/a_2$ . For the soil plug this region of sharp decrease in the activity coefficient is characterized by the sudden decrease in the e.m.f. The accompanying curve shows the behavior of a hypothetical membrane. All membranes have a range of concentration of solution where they behave as an ideal permselective membrane. Here the transport number of ionic species (with respect to which the particular membrane is permselective) is one and hence the membrane behaves as a reversible electrode. The e.m.f. at this range of concentration has a highest theoretical maximum value given by the Nernst equation. However, as the solution becomes more dilute the e.m.f. developed becomes less than that predicted by the Nernst equation. This has been considered to be due to the hydrolysis of the membrane. The present study points out that there is not only hydrolysis of the soil clays but also a much lower activity of whatever counterions still remain in the clay micelle. This decrease in e.m.f.



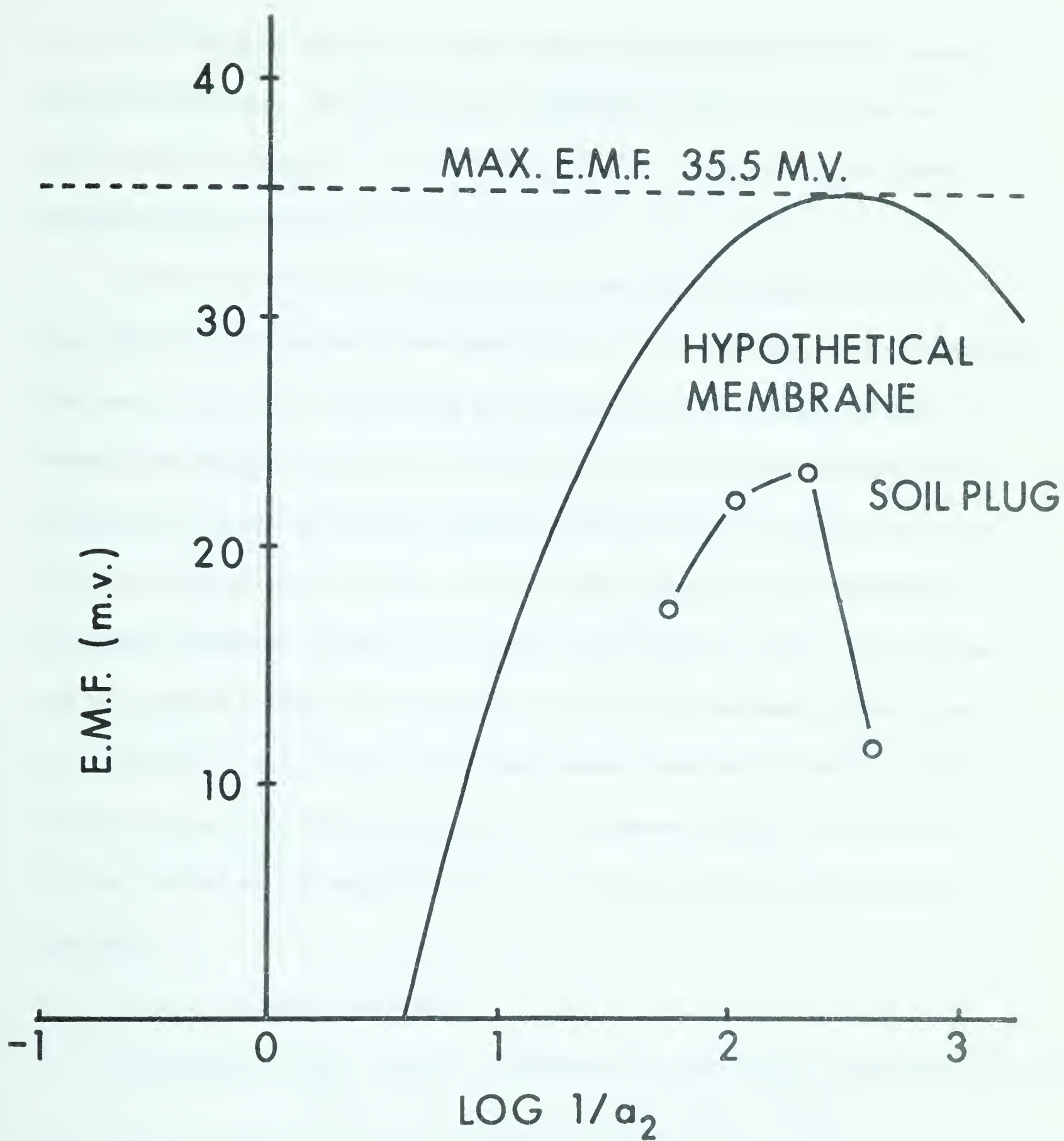


FIG. 16 CELL E.M.F. AND  $\text{LOG } 1/a_2$   
WHERE  $a_1/a_2 = 2$

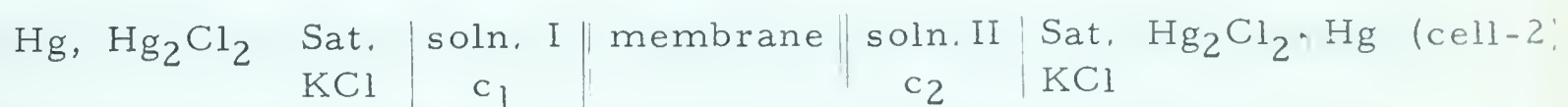




for the soil plug is seem to be more sharp than that found in the conventional membranes. Had the activity coefficient of the counterion not decreased so suddenly, it would seem that the e.m.f. of the soil plug would have reached the theoretical maximum value.

The permselective behavior of a membrane is approximately described by the Teorell-Myers and Sievers theory of membrane potentials. Because of the many simplifying assumptions as described in chapter 1, membranes seldom obey the Teorell-Myers and Sievers equation exactly. However, in order to test the validity of the theory for a particular membrane one can obtain the value of  $A$ , the fixed charge of the membrane, by a graphical method, described by Meyer and Sievers (1936). This value can be compared with the independently obtainable exchange capacity of the membrane. For most of the membranes these two values are found to be of the same order of magnitude. The above graphical method in addition furnishes the mobility ratio of the cation and the anion in the membrane.

For a concentration cell



the e.m.f. is given by a modified form of Equ. 1-48, where ideal conditions are assumed. This is the Meyer-Sievers equation

$$E = \frac{RT}{F} \left[ u' \ln \frac{x_2 + \bar{A}u'}{x_1 + \bar{A}u'} + \ln \frac{(x_1 + A)(x_2 - \bar{A})}{(x_1 - \bar{A})(x_2 + \bar{A})} \right] \quad (1-48a)$$

where  $u' = (u_+ - u_-)/(u_+ + u_-)$ , the mobility ratio;  $x = \sqrt{4c^2 + \bar{A}^2}$  and  $\bar{A}$  is the fixed charge of the membrane. Modification of the above equation gives



$$E = \frac{RT}{F} \left[ \frac{u' \ln \frac{x_2 + u'}{\bar{A}} + \ln \frac{(x_1 + 1)(x_2 - 1)}{\bar{A}}}{\frac{x_1 + u'}{\bar{A}}} \right] \quad (1-48b)$$

where  $E$  depends only on  $u'$ ,  $x_1/\bar{A}$  and  $x_2/\bar{A}$ . If a constant ratio of  $c_1/c_2 = 2$  is utilized, it is possible to draw a series of curves for  $E$ , the e.m.f. and  $\log \bar{A}/c_2$ , for values of  $u'$  between  $-1 < u' < +1$ . These curves are shown in Fig. 17. If the experimental values of  $E$  (with constant ratio of  $c_1/c_2 = 2$ ) are plotted against  $\log 1/c_2$  and if the membrane follows the theory, then the shape of the resultant curve should resemble one of the theoretical curves. Since on a log scale multiplication of two numbers becomes addition,  $\log \bar{A}/c_2 = \log \bar{A} + \log 1/c_2$ . Thus the displacement of the experimental curve in matching it with one of the theoretical curves should represent  $\log \bar{A}$ . This value of  $\bar{A}$  can then be compared with the independently determined value of the exchange capacity.

For the soil plug the points are shown in Fig. 17. It is realized that the number of points are not adequate to fix the shape of the curve, however, since the range of concentrations of solution where the specific influence of the soil phase is predominant, is so small that only four points with  $c_1/c_2$  could be obtained. Three of these are shown (the fourth one has been shown in Fig. 16). The experimental curve when displaced to the left (negative direction) by 0.9 units would approximately overlap the theoretical curve of  $u_+/u_- = 0.14$ . Thus  $\log \bar{A} = -0.9$  and  $\bar{A}$  would be equal to 0.13 molal. It is known from independent measurements that  $\bar{A} = 0.14$  molal. Thus in as much as the above graphical method is





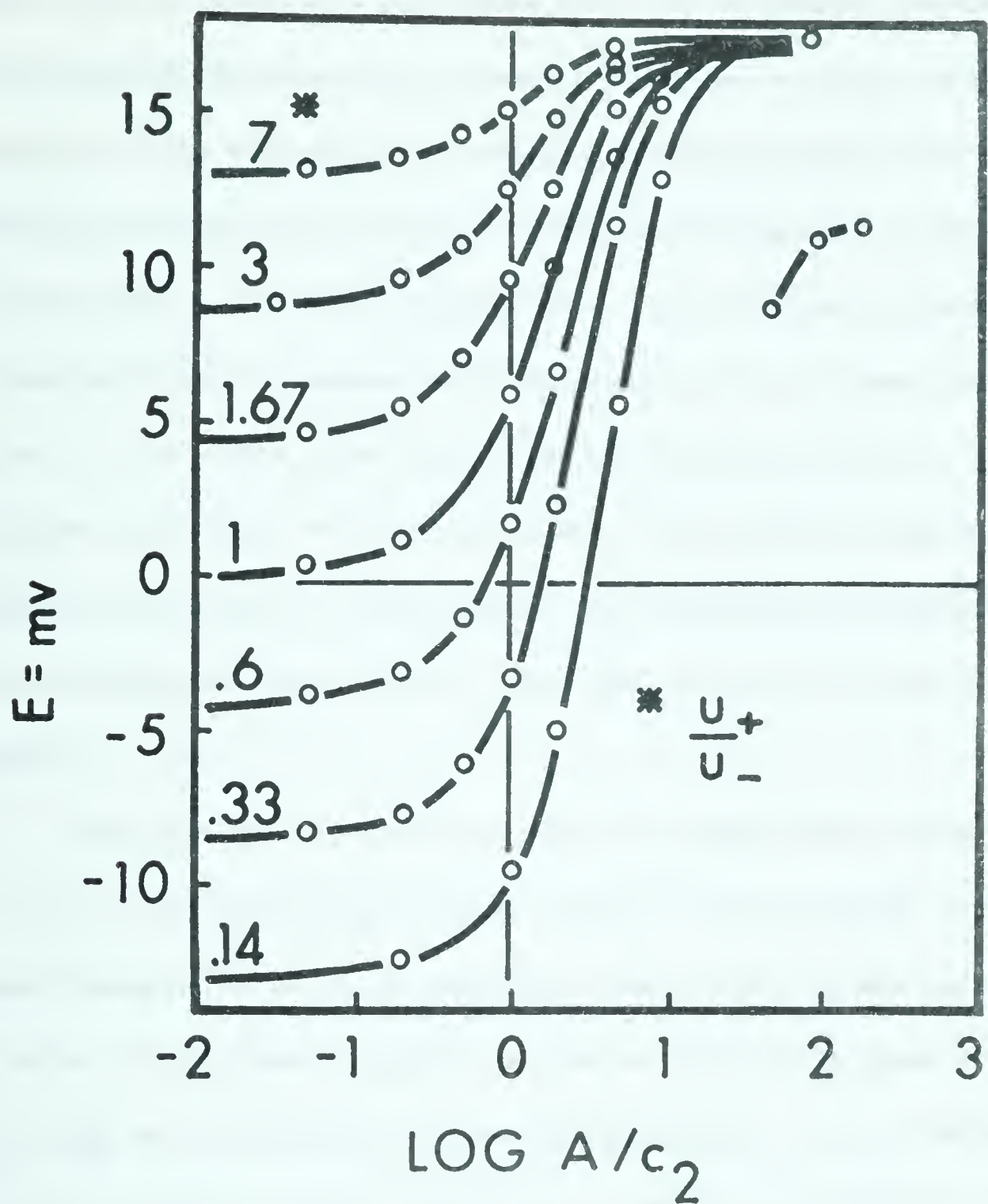


FIG. 17 THEORETICAL CURVES OF MYERS AND SIEVERS EQUATION AND THE EXPERIMENTAL POINTS FOR SOIL PLUG



approximate, the above agreement of the experimental points for the soil plug with the theoretical curve is sufficient evidence to the general behavior of the soil plug as a membrane (though imperfect). The fact that the mobility of the cation over this permselective range is only 0.14 of that of the anion is also significant. For the actual mobilities determined by transport number and conductance measurement this ratio  $u_+/u_- = 0.14$ . This proves that over the range of 0.0080 to 0.016 m solution, soil plugs would transfer the cations preferentially and their behavior is similar to membranes. The potentials developed over this range are approximately those predicted by Teorell-Myers and Sievers theory.

The findings of this study should be applicable to other soils which would vary in the amount of fixed charge or the exchange capacity. The fixed charge  $\bar{A}$  is the most important factor affecting the electrochemistry of soils. If the fixed charge  $\bar{A}$  is greater than in the present case (0.14 m) the range of concentration where that particular soil will behave as permselective would be higher than in the present case (0.0080 - 0.0160). Since  $\bar{A}$  is expressed as moles/Kgm. of soil, its value would be halved for a divalent cation and thus the permselective range of concentration is expected to be (approximately) halved also. Since naturally occurring soils such as Ponoka loam are essentially calcium systems (about 60% fixed charge satisfied by  $\text{Ca}^{++}$ ) the permselective range of concentration is expected to be around 0.004 to 0.008 m. From data of Anderson et al. (1942) for a Barnes Loam soil South Dakota (79% fixed charge satisfied by



$\text{Ca}^{++}$ ) the minimum solution phase concentration of  $\text{Ca}^{++}$  at saturation can be shown to be 0.003 equivalent, i. e. 0.002 molar. For the quantity of soluble salts present in any soil, the solution phase concentration would be least when all the pore space is occupied by water. The solution phase would become concentrated as a result of evaporation of water. As pointed out before, above a certain concentration range the transport numbers of cations and anions in the soil phase are expected to approach those in the solution phase. Thus in a saturated state (when most of the pore space is occupied by solution) the natural soil would invariably transfer cations selectively over anions, if its solution concentration is in a particular range. If below this, anions will be selectively transferred. With progressive increase in concentration of solution phase on dehydration, the transport numbers of cations and anions are expected to approach their value in solution. Establishment of equilibrium between the soil phase and solution phase would be limited only by the rate of diffusion, exchange reactions being much faster.





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## APPENDIX

### 1. Physical and Chemical properties of ion exchangers used -

#### a. Ponoka Loam

(i) C.E.C. with organic matter -  $44 \pm 0.5$  me. per 100 gm.

without organic matter -  $17 \pm 0.05$  me. per 100 gm.

#### (ii) Physical properties

organic matter -  $15 \pm 1\%$  of the total weight.

clay (below 0.002 mm. size) - 28%.

silt (0.050 - 0.002 mm. size) - 69%.

sand (0.050 - 2.00 mm.) 3%.

Ponoka loam is a misnomer, and on the basis of the

mechanical analysis, above soil would be Silty clay loam.

(iii) Surface area -  $82 \text{ m}^2/\text{gm.}$  of soil.

#### b. Dowex 50W - X8

(i) C.E.C. (dry basis) - 4.9 me. per gm.

#### c. Bentonite clay

(i) C.E.C. - 110 me. per 100 gm.

#### d. Kaolinite - 3 me. per 100 gm.



2. Self-diffusion coefficients of  $\text{Rb}^+$  and  $\text{Cl}^-$  in soil ( $10^3 \times \text{cm}^2/\text{hr.}$ )

| Treatment |                 | Temperature (°C) |              |             |
|-----------|-----------------|------------------|--------------|-------------|
|           |                 | 20 ± 0.1         | 25 ± 0.1     | 30 ± 0.1    |
| I         | Rb <sup>+</sup> | 2.36 ± 0.13      | 1.63 ± 0.06  | 3.86 ± 0.35 |
|           | Cl <sup>-</sup> | 8.84 ± 0.37      | 16.97 ± 1.36 | -           |
| II        | Rb <sup>+</sup> | 2.12 ± 0.11      | 1.63 ± 0.06  | 3.26 ± 0.05 |
|           | Cl <sup>-</sup> | 7.58 ± 0.68      | 26.52 ± 3.32 | -           |
| III       | Rb <sup>+</sup> | 1.01 ± 0.02      | 1.06 ± 0.03  | 1.25 ± 0.02 |
|           | Cl <sup>-</sup> | 1.70 ± 0.07      | 28.29 ± 3.77 | -           |

3. Self-diffusion coefficients for packings of glass beads and sand (0.01 N  $\text{RbCl}$ )

A. When pH was 3.0

I - 50 micron glass beads. Pore fraction 0.48.

$\text{Rb}^{86} - 1.3 \pm 0.3 \times 10^{-2} \text{ cm}^2/\text{hr.}$

$\text{Cl}^{36} - 4.0 \pm 0.4 \times 10^{-2} \text{ cm}^2/\text{hr.}$

II - 140-210 micron glass beads. Pore fraction 0.37.

$\text{Rb}^{86} - 1.9 \pm 0.1 \times 10^{-2} \text{ cm}^2/\text{hr.}$

$\text{Cl}^{36} - 4.2 \pm 0.2 \times 10^{-2} \text{ cm}^2/\text{hr.}$

III - 35 mesh sand. Pore fraction 0.31.

$\text{Rb}^{86} - 3.3 \pm 0.1 \times 10^{-2} \text{ cm}^2/\text{hr.}$

$\text{Cl}^{36} - 3.6 \pm 0.2 \times 10^{-2} \text{ cm}^2/\text{hr.}$

B. When pH was  $6.5 \pm 0.2$ .

I - 50 micron glass beads. Pore fraction 0.48.

$\text{Rb}^{86} - 1.4 \pm 0.1 \times 10^{-2} \text{ cm}^2/\text{hr.}$

$\text{Cl}^{36} - 1.6 \pm 0.2 \times 10^{-2} \text{ cm}^2/\text{hr.}$

II - 140-210 micron glass beads. Pore fraction 0.37.

$\text{Rb}^{86} - 2.0 \pm 0.2 \times 10^{-2} \text{ cm}^2/\text{hr.}$

$\text{Cl}^{36} - 2.3 \pm 0.1 \times 10^{-2} \text{ cm}^2/\text{hr.}$



#### 4. Mean molal activity coefficients

|                                                 | 1      | 2      | 3      | 4      | 5      | 6      |
|-------------------------------------------------|--------|--------|--------|--------|--------|--------|
| Conc. Soln. Phase<br>(molal)                    | 0.0005 | 0.0010 | 0.0050 | 0.0102 | 0.0213 | 0.0445 |
| Rb <sup>+</sup> Soil Phase<br>(moles/Kgm. soil) | 0.0435 | 0.0069 | 0.1215 | 0.1387 | 0.1891 | 0.2687 |
| Cl <sup>-</sup> Soil Phase<br>(moles/Kgm. soil) | 0.0011 | 0.0021 | 0.0039 | 0.0105 | 0.0221 | 0.0463 |
| $\gamma_{\pm}$ Soil Phase                       | 0.0705 | 0.0815 | 0.2127 | 0.2400 | 0.2835 | 0.3258 |
| $\gamma_{\pm}$ Soln. Phase                      | 0.9747 | 0.9449 | 0.9260 | 0.8991 | 0.8635 | 0.8185 |

#### 5. Modified D.C. conductance procedure

Resistance measurements in Perspex cell (Platinized - Pt. electrodes of 20 cm<sup>2</sup> area; temperature 25 ± 0.1°C; current density 0.0428 me/cm<sup>2</sup>).

| Successive<br>Measurements  | Cell Resistance<br>(ohms)                 | Precision of a. c.<br>Resistance Measurements |
|-----------------------------|-------------------------------------------|-----------------------------------------------|
| 0.01 N KCl Solution in Cell |                                           |                                               |
| 1. a. c.                    | (a) 522.881<br>(b) 522.217<br>(c) 522.722 | ± 0.0635%                                     |
| 2. d. c.                    | 530.300                                   |                                               |
| 3. a. c.                    | (a) 522.663<br>(b) 522.999                | ± 0.0322%                                     |
| 4. d. c.                    | 529.030                                   |                                               |
| 5. a. c.                    | (a) 522.920<br>(b) 522.891                | ± 0.0029%                                     |

Precision of d. c. resistance measurement: ± 0.12%

Literature value of K<sub>sp</sub>: 0.0014115

K<sub>sp</sub> with d. c. resistance: (i) cell constant 0.75 - 0.0014160

(accuracy - 0.32% higher)

(ii) cell constant 0.737822 - 0.0013930

(accuracy - 1.3% lower)

K<sub>sp</sub> with a. c. resistance: (i) cell constant 0.75 - 0.0014346

(accuracy - 1.7% higher)

(ii) cell constant 0.737822 - 0.0014115

(basis of cell constant calculation)





5. Modified D. C. conductance procedure (continued)

| Successive Measurements                                 | Cell Resistance (Ohms)                    | Precision of a. c. Resistance Measurements |
|---------------------------------------------------------|-------------------------------------------|--------------------------------------------|
| 0.01 N Na <sub>2</sub> SO <sub>4</sub> Solution in Cell |                                           |                                            |
| 1. a. c.                                                | (a) 631.741<br>(b) 532.202<br>(c) 631.414 | ± 0.062%                                   |
| 2. d. c.                                                | 641.705                                   |                                            |
| 3. a. c.                                                | (a) 632.226<br>(b) 631.921<br>(c) 632.023 | ± 0.024%                                   |
| 4. d. c.                                                | 641.660                                   |                                            |
| 5. a. c.                                                | (a) 631.850<br>(b) 632.315                | ± 0.037%                                   |

Precision of d. c. resistance measurement: ± 0.003%

Literature value of Ksp: 0.0011244

Ksp with d. c. resistance: (i) cell constant 0.75 - 0.0011688  
(accuracy 4% higher)

(ii) cell constant 0.737822 - 0.0011498  
(accuracy 2.3% higher)

Ksp with a. c. resistance (i) cell constant 0.75 - 0.0011868  
(accuracy 5.5% higher)

(ii) cell constant 0.737822 - 0.0011675  
(accuracy 3.9% higher)



5. Modified D. C. conductance procedure (continued)

| Successive<br>Measurements                             | Cell Resistance<br>(ohms)                                | Precision of a. c.<br>Resistance Measurements |
|--------------------------------------------------------|----------------------------------------------------------|-----------------------------------------------|
| 0.1 N Na <sub>2</sub> SO <sub>4</sub> Solution in Cell |                                                          |                                               |
| 1. a. c.                                               | (a) 80.4195<br>(b) 79.9372<br>(c) 80.2257<br>(d) 79.5245 | ± 0.55%                                       |
| 2. d. c.                                               | 90.7962                                                  |                                               |
| 3. a. c.                                               | (a) 79.6515<br>(b) 80.3008<br>(c) 79.8293<br>(d) 80.1884 | ± 0.41%                                       |
| 4. d. c.                                               | 90.8850                                                  |                                               |
| 5. a. c.                                               | (a) 80.5008<br>(b) 80.1666<br>(c) 80.4850                | ± 0.21%                                       |

Precision of d. c. resistance measurements: ± 0.049%

Literature Ksp: 0.008998

Ksp with d. c. resistance (i) cell constant 0.75 - 0.0082562

(accuracy 8.3% lower)

(ii) cell constant 0.737822 - 0.0081222

(accuracy 9.7% lower)

Ksp with a. c. resistance (i) cell constant 0.75 - 0.0093619

(accuracy 4.0% higher)

(ii) cell constant 0.737822 - 0.0092099

(accuracy 2.4% higher)





# 5. Modified D. C. conductance procedure (continued)

## Effect of orientation of Phillips cell

0.01 N KCl solution;  $25^{\circ} \pm 0.1^{\circ}\text{C}$ ; Phillips cell PR9510/00 with cell constant 1.54; area of electrode  $0.81\text{ cm}^2$ ; current density  $36.2\text{ me./cm.}^2$ .

| Current used | Cell Resistance<br>(ohms) |
|--------------|---------------------------|
|--------------|---------------------------|

### Cell vertical

|    |       |       |
|----|-------|-------|
| 1. | a. c. | 459   |
| 2. | d. c. | 696.7 |
| 3. | a. c. | 459   |
| 4. | d. c. | 696.2 |
| 5. | a. c. | 459   |

Precision of d. c. resistance measurements:  $\pm .036\%$

Precision of a. c. resistance measurements: Reproduce literature values to limit of bridge accuracy  $\pm 1\%$

Accuracy of d. c. resistance measurements: 8.15% higher

### Cell + $45^{\circ}$ from vertical

|    |       |       |
|----|-------|-------|
| 1. | a. c. | 459   |
| 2. | d. c. | 683.3 |
| 3. | a. c. | 459   |

Change in d. c. specific conductance with orientation: 1.89% higher

### Cell - $45^{\circ}$ from vertical

|    |       |       |
|----|-------|-------|
| 1. | d. c. | 684.9 |
| 2. | a. c. | 459   |

Change in d. c. specific conductance: 1.8% higher



## 6. Calculation of Friction and Phenomenological Coefficients\*

The bulk density is 0.92, i.e. 0.92 gms. of soil per ml.

$$c_1 = 0.1276 \times 10^{-3} \text{ moles cm}^{-3}$$

$$c_2 = 0.9907 \times 10^{-3} \text{ moles cm}^{-3}$$

$$c_3 = 3.61 \times 10^{-2} \text{ moles cm}^{-3}$$

$$\text{Volumetric moisture content} = 0.65 \text{ i.e. } 0.65 \frac{\text{gms.}}{\text{ml.}}$$

$$\frac{6.5 \times 10^{-1}}{18} = 3.61 \times 10^{-2}$$

$$D_1 = 6.56 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1} \quad k = 1.60 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$D_2 = 2.46 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \quad t^+ = 0.65$$

$$\text{water transport (W - H)} = (24.16 - 3) = 21.16$$

$$a \equiv \frac{RT}{D_1} = X_{13} + X_{14}$$

$$\begin{aligned} &= \frac{8.315 \times 298}{6.56 \times 10^{-7}} = \frac{8.315 \times 2.98 \times 10^2}{6.56 \times 10^{-7}} = \frac{24.7787 \times 10^2}{6.56 \times 10^{-7}} \\ &= 3.77 \times 10^9 = \frac{(G_{13} + G_{14})}{X_{13} + X_{14}} \end{aligned}$$

$$b = \frac{RT}{D_2} = \frac{24.7787 \times 10^2}{2.46 \times 10^{-6}} = 10.07 \times 10^8 = 1.01 \times 10^9 = \frac{(G_{23} + G_{24})}{X_{23} + X_{24}}$$

$$\begin{aligned} A &= \frac{K}{F^2} = \frac{1.60 \times 10^{-3}}{9.31 \times 10^9} = 0.172 \times 10^{-12} \\ &= 1.72 \times 10^{-13} \end{aligned}$$

$$B = \frac{(W - H)k}{c_3 F^2} = \frac{21.16 \times 1.60 \times 10^3}{3.61 \times 10^{-2} \times 9.31 \times 10^9} = \frac{33.856 \times 10^{-3}}{33.609 \times 10^7} = 1.01 \times 10^{-10}$$

$$\begin{aligned} c &= \frac{t^+ k}{c_1 F^2} = \frac{0.65 \times 1.60 \times 10^{-3}}{1.276 \times 10^{-4} \times 9.31 \times 10^9} = \frac{1.04 \times 10^{-3}}{11.88 \times 10^5} \\ &= \frac{1.04 \times 10^{-3}}{1.188 \times 10^6} = 0.875 \times 10^{-9} \\ &= 8.75 \times 10^{-10} \end{aligned}$$

\* See chapter 5 for explanation for equations used.



$$\begin{aligned} \frac{(G_{13})}{X_{13}} &= \frac{(aC - 1)}{B} \\ &= \frac{3.77 \times 10^9 \times 8.75 \times 10^{-10} - 1}{1.01 \times 10^{-10}} = \frac{3.299 - 1}{1.01 \times 10^{-10}} = \frac{2.299}{1.01 \times 10^{-10}} \\ &= 2.276 \times 10^{10} \end{aligned}$$

$$\frac{(G_{13})}{X_{13}} = (W \text{ sec}^2 \text{ cm}^{-2} \text{ mole}^{-1}) = 2.28 \times 10^{10}$$

$$\begin{aligned} \frac{(G_{23})}{X_{23}} &= \frac{c_1 b}{c_2 B} \quad C - \frac{A}{c_1} + \frac{c_2}{1 b} \\ &= \frac{1.276 \times 10^{-4} \times 1.01 \times 10^9}{9.7 \times 10^{-6} \times 1.01 \times 10^{-10}} \quad 8.75 \times 10^{-10} - \frac{1.72 \times 10^{-13}}{1.276 \times 10^{-4}} + \frac{9.7 \times 10^{-6}}{1.276 \times 10^{-4} \times 1.01 \times 10^9} \\ &= \frac{1.289 \times 10^5}{9.80 \times 10^{-16}} \quad 8.75 \times 10^{-10} - 1.35 \times 10^{-9} + \frac{9.7 \times 10^{-6}}{1.289 \times 10^5} \\ &= 1.32 \times 10^{20} \quad 8.75 \times 10^{-10} - 13.5 \times 10^{-10} + 7.53 \times 10^{-11} \\ &= 1.32 \times 10^{20} \quad \frac{8.75 \times 10^{-10} - 13.5 \times 10^{-10} + 0.753 \times 10^{-10}}{9.50} \\ &= 1.32 \times 10^{20} \quad -4.0 \times 10^{-10} = -5.28 \times 10^{10} \end{aligned}$$

$$\frac{(G_{23})}{X_{23}} = -5.28 \times 10^{10}$$

$$\begin{aligned} \frac{(G_{13})}{X_{13}} + \frac{(G_{14})}{X_{14}} &= 3.77 \times 10^9 \\ \therefore X_{14} &= 3.77 \times 10^9 - 2.28 \times 10^{10} \\ &= 3.77 \times 10^{10} - 2.28 \times 10^{10} \end{aligned}$$

$$\therefore \frac{(G_{14})}{X_{14}} = -1.90 \times 10^{10}$$





Similarly

$$\begin{aligned} (G_{24}) \\ X_{24} &= 1.01 \times 10^9 + 5.28 \times 10^{10} \\ &= 0.101 \times 10^{10} + 5.28 \times 10^{10} \end{aligned}$$

$$\therefore X_{24} = 5.38 \times 10^{10}$$

$$\begin{aligned} X_{13}^2 (-c_1 bC) + X_{13} c_1 b(aC - 1) + X_{23}^2 -c_2(aC - 1) + X_{23} c_2 b(aC - 1) \\ \text{I} \qquad \qquad \qquad \text{II} \qquad \qquad \qquad \text{III} \qquad \qquad \qquad \text{IV} \\ + X_{13} X_{23} c_2 + X_{34} c_3 b(aC - 1) = 0 \\ \text{V} \qquad \qquad \qquad \text{VI} \end{aligned}$$

$$\begin{aligned} (2.28 \times 10^{10})^2 (-1.276 \times 10^{-4} \times 1.01 \times 10^9 \times 8.75 \times 10^{-10}) \\ = 5.20 \times 10^{20} (-1.13 \times 10^{-4}) = -5.88 \times 10^{16} \text{ ----- I} \\ 2.28 \times 10^{10} \quad 1.289 \times 10^5 (2.299) = 2.28 \times 10^{10} \quad 2.96 \times 10^5 = 6.75 \times 10^{15} \text{ ---- II} \\ 27.88 \times 10^{20} \quad -9.7 \times 10^6 (2.299) = 2.788 \times 10^{21} \quad -2.23 \times 10^{-5} \\ = -6.22 \times 10^{16} \text{ ----- III} \\ -5.28 \times 10^{10} \quad 9.7 \times 1.01 \times 10^9 \times 2.299 = -5.28 \times 10^{10} \quad 22.52 \times 10^3 \\ = -11.89 \times 10^{14} = -1.19 \times 10^{15} \text{ ----- IV} \\ 2.28 \times 10^{10} \times (-5.28 \times 10^{10}) \times 9.7 \times 10^{-3} = 116.77 \times 10^{17} \\ = 1.17 \times 10^{19} \text{ ----- V} \end{aligned}$$

$$X_{34} \times 3.61 \times 10^{-2} \times 1.01 \times 10^9 \times 2.299 = X_{34} (8.38 \times 10^7)$$

$$\begin{aligned} \therefore -X_{34} (8.38 \times 10^7) &= -5.88 \times 10^{16} + 6.75 \times 10^{15} - 6.22 \times 10^{16} \\ &\quad - 1.19 \times 10^{15} - 1.17 \times 10^{19} \end{aligned}$$

$$= -12.22 \times 10^{16} + 0.675 \times 10^{16} + 1.17 \times 10^{19}$$

$$= -1.15 \times 10^{17} - 116.77 \times 10^{17} - 116.77 \times 10^{17} = -1.17 \times 10^{19}$$



$$\therefore \overset{(G_{34})}{X_{34}} = \frac{1.17 \times 10^{19}}{8.38 \times 10^7} = 0.1396 \times 10^{12} = 1.40 \times 10^{11}$$

$$\therefore \overset{(G_{34})}{X_{34}} = 1.40 \times 10^{11}$$

$$X_{13} = 2.28 \times 10^{10}; \quad X_{23} = -5.28 \times 10^{10}; \quad X_{14} = -1.90 \times 10^{10}$$

$$X_{24} = 5.38 \times 10^{10}; \quad X_{34} = 1.40 \times 10^{11}$$

- Phenomenological Coefficients -

$$d = \underset{\text{I}}{c_1 X_{13} X_{14} (X_{23} + X_{24})} + \underset{\text{II}}{c_2 X_{23} X_{24} (X_{13} + X_{14})} + \underset{\text{III}}{c_3 X_{34} (X_{13} + X_{14}) (X_{23} + X_{24})}$$

$$= 1.276 \times 10^{-4} \times 2.28 \times 10^{10} (-1.90 \times 10^{10}) (1.01 \times 10^9) = -5.58 \times 10^{25} \text{ ----- I}$$

$$\frac{9.7 \times 10^{-6} \times (-5.28 \times 10^{10}) (5.38 \times 10^{10}) (3.77 \times 10^9)}{5.12 \times 10^5} = -1.04 \times 10^{26} \text{ ----- II}$$

$$\frac{3.61 \times 10^{-2} \times 1.40 \times 10^{11} \times 3.77 \times 10^9 \times 1.01 \times 10^9}{5.05 \times 10^9} = 19.24 \times 10^{27}$$

$$3.81 \times 10^{18}$$

$$= 1.92 \times 10^{28} \text{ ----- III}$$

$$\therefore d = -5.58 \times 10^{25} - 1.04 \times 10^{26} + 1.92 \times 10^{28} = 1.90 \times 10^{28}$$

$$0.016 \times 10^{28}$$

$$L_{11} = \frac{c_1}{d} c_1 X_{13} + c_3 X_{34} X_{23} + X_{24} + c_2 X_{23} X_{24}$$

$$= \frac{1.276 \times 10^{-4}}{1.90 \times 10^{28}} (1.276 \times 10^{-4} \times 2.28 \times 10^{10} + 3.61 \times 10^{-2} \times 1.40 \times 10^{11})$$

$$(1.01 \times 10^9) + 9.7 \times 10^6 \times (-5.28 \times 10^{10}) (5.38 \times 10^{10})$$

$$5.122 \times 10^5$$

$$= 0.672 \times 10^{-32} (2.91 \times 10^6 + 5.05 \times 10^{11}) (1.01 \times 10^9) - 2.76 \times 10^{16}$$

neglect



$$= 0.672 \times 10^{-32} \quad 5.10 \times 10^{20} - 2.76 \times 10^{16} \quad = 3.43 \times 10^{-12} = L_{11}$$

neglect

$$L_{22} = \frac{c_2}{d} (c_2 X_{23} + c_3 X_{34}) (X_{13} + X_{14}) + c_1 X_{13} X_{14}$$

$$= \frac{9.7 \times 10^{-6}}{1.90 \times 10^{28}} (9.7 \times 10^{-6} \times -5.28 \times 10^{10} + 3.61 \times 10^{-2} \times 1.40 \times 10^{11}) (3.77 \times 10^9)$$

$$\quad \quad \quad -51.22 \times 10^4 \quad \quad \quad 5.05 \times 10^9$$

neglect

$$+ 1.276 \times 10^4 \times 2.28 \times 10^{10} \times (-1.90 \times 10^{10})$$

$$= 5.11 \times 10^{34} \quad 1.90 \times 10^{19} - 5.53 \times 10^{16} \quad = 9.71 \times 10^{-15} = L_{22}$$

neglect

$$L_{12} = L_{21} = \frac{c_1}{d} c_2 X_{13} X_{23}$$

$$= 0.672 \times 10^{-32} \times 9.7 \times 10^{-6} \times 2.28 \times 10^{10} \times -5.28 \times 10^{10}$$

$$\quad \quad \quad 6.52 \times 10^{-38} \quad \quad \quad -12.04 \times 10^{20} \quad \quad \quad 1.20 \times 10^{21}$$

$$= -7.82 \times 10^{-17} = L_{12} = L_{21}$$

$$L_{23} = L_{32} = \frac{c_2}{d} c_3 (X_{13} + X_{14}) X_{23}$$

$$= 5.11 \times 10^{34} \times 3.61 \times 10^{-2} \times 3.77 \times 10^9 \times -5.28 \times 10^{10}$$

$$\quad \quad \quad 1.84 \times 10^{-35} \quad \quad \quad -1.99 \times 10^{20}$$

$$= -3.66 \times 10^{-15} = L_{23} = L_{32}$$

$$L_{13} = L_{31} = \frac{c_1}{d} c_3 X_{13} (X_{23} + X_{24})$$

$$= 0.672 \times 10^{-32} \times 3.61 \times 10^{-2} \times 2.28 \times 10^{10} (1.01 \times 10^9)$$

$$\quad \quad \quad 2.30 \times 10^{19}$$

$$= 2.43 \times 10^{-34} \times 2.30 \times 10^{19} = 5.59 \times 10^{-15} = L_{13} = L_{31}$$

$$L_{33} = \frac{c_3^2}{d} (X_{13} + X_{14}) (X_{23} + X_{24})$$

$$= \frac{1.30 \times 10^{-3}}{1.90 \times 10^{28}} \times 3.77 \times 10^9 \times 1.01 \times 10^9$$





$$= 0.684 \times 10^{-31} \times 3.81 \times 10^{18} = 2.61 \times 10^{-13} = L_{33}$$

$$L_{11} = 3.43 \times 10^{-12}; L_{22} = 9.71 \times 10^{-15}; L_{12} = -7.82 \times 10^{-17} = L_{21}$$

$$L_{23} = L_{32} = -3.66 \times 10^{-15}; L_{13} = L_{31} = 5.59 \times 10^{-15}; L_{33} = 2.61 \times 10^{-13}$$

$$J_1 = 3.43 \times 10^{-12} X_1 - 7.82 \times 10^{-17} X_2 + 5.59 \times 10^{-15} X_3$$

$$J_2 = -7.82 \times 10^{-17} X_1 + 9.71 \times 10^{-15} X_2 - 3.66 \times 10^{-15} X_3$$

$$J_3 = 5.59 \times 10^{-15} X_1 - 3.66 \times 10^{-15} X_2 - 2.61 \times 10^{-13} X_3$$

$$X_{13}^o = \frac{RT}{D_1^o} = \frac{24.7787 \times 10^2}{2.07 \times 10^{-5}} = 1.20 \times 10^8$$

$$X_{23}^o = \frac{RT}{D_2^o} = \frac{24.7787 \times 10^2}{2.03 \times 10^{-5}} = 1.22 \times 10^8$$

For soil

$$\frac{c_3}{c_1} = 282.9 \quad \frac{X_{34}}{X_{13}} = 6.14$$

From Spiegler table 1

$$\frac{c_3}{c_1} = 25.58 \quad \frac{X_{34}}{X_{13}} = \frac{4.8 \times 10^6}{2.59 \times 10^8} = 1.85 \times 10^{-2}$$

## 7. List of symbols

A Area (cm<sup>2</sup>)

$\bar{A}$  Fixed charge on an exchanger (mole kgm<sup>-1</sup>)

a Activity (mole kgm<sup>-1</sup>)

c Concentration (mole liter<sup>-1</sup>)

D Diffusion coefficient (cm<sup>2</sup>sec<sup>-1</sup>) Barred quantities refer to the diffusion coefficient in porous medium while superscript zero refers to Nernst-limiting value.



|                 |                                                           |
|-----------------|-----------------------------------------------------------|
| E               | Electromotive force (volt).                               |
| e               | electronic charge (coulomb).                              |
| F               | Faraday (coulomb equiv. $^{-1}$ ).                        |
| F               | Gibbs Free Energy (Wsec mole $^{-1}$ )                    |
| $f_{\pm}$       | Mean rational activity coefficient.                       |
| $G_{ij}$        | Friction coefficient (Wsec $^2$ cm $^{-2}$ mole $^{-1}$ ) |
| h               | Labyrinth or tortuosity factor.                           |
| I               | Current (amp. )                                           |
| J               | Flux (mole cm $^{-2}$ sec $^{-1}$ ).                      |
| K <sub>sp</sub> | Specific conductance (Ohm $^{-1}$ cm $^{-1}$ ).           |
| k               | Boltzman constant (Wsec deg $^{-1}$ ).                    |
| L               | Macroscopic distance (cm. ).                              |
| L <sub>e</sub>  | Actual distance travelled by ion in porous medium (cm. )  |
| m               | Concentration (mole kgm. $^{-1}$ )                        |
| N               | Avogadro's number (molecule mole $^{-1}$ ).               |
| n               | Moles                                                     |
| P               | Pressure (Wsec cm $^{-3}$ ).                              |
| R               | Gas constant (Wsec deg $^{-1}$ mole $^{-1}$ ).            |
| S               | Entropy (Wsec deg $^{-1}$ ).                              |
| T               | Absolute temperature (deg. ).                             |
| t               | time (sec. ).                                             |
| U               | Internal energy (Wsec mole $^{-1}$ ).                     |
| $U_i$           | Mobility (mole cm $^2$ sec $^{-1}$ wattsec $^{-1}$ ).     |
| $u_i$           | Mobility (cm $^2$ volt $^{-1}$ sec $^{-1}$ ).             |



- V Volume ( $\text{cm}^3$ ).
- $v_i$  Velocity ( $\text{cm. sec}^{-1}$ ).
- W mobility ( $\text{cm. sec}^{-1}\text{dyne}^{-1}$ ).
- x Distance coordinate (cm. ).
- z Valence.
- $\gamma_{\pm}$  Mean molal activity coefficient.
- $\epsilon$  Pore fraction.
- $\epsilon'$  Dielectric constant.
- $\theta$  Angle.
- $\bar{\theta}$  Volumetric solution content.
- $\kappa$  Ionic parameter.
- $\lambda$  Distance between equilibrium position.
- $\lambda$  Ionic conductance ( $\text{Ohm}^{-1}\text{cm}^2\text{equiv.}^{-1}$ ).
- $\mu$  Chemical potential ( $\text{Wsec. mole}^{-1}$ ).
- $\rho$  Resistivity ( $\text{Ohm cm.}$  ).
- $\tau$  Oscillation time ( $\text{sec}^{-1}$ ).
- $\psi$  Potential (volt).









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